

THREE NEW TECHNIQUES FOR FLOATING POLLUTANT
SPILL CONTROL AND RECOVERY

by

William W. Bannister and Alfred H. Donatelli
University of Lowell
Lowell, Massachusetts 01854

William A. Curby
Sias Laboratories, Lahey Clinic Foundation
Burlington, Massachusetts 01803

David L. Kan
Massachusetts Maritime Academy
Buzzards Bay, Massachusetts 02532

William J. Dalton and David A. Porta
Datasonics, Inc.
Cataumet, Massachusetts 02534

Grant Nos. R-806118-01 and R-804628-01

Project Officer

Uwe Frank
Oil and Hazardous Materials Spills Branch
Municipal Environmental Research Laboratory - Cincinnati
Edison, New Jersey 08837

MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Grant Nos. R-806118-01 and R-804628-01 to the University of Lowell. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This report discusses three new techniques of oil and floating hazardous material spill control and recovery whereby (1) spills can be gelled to a solid consistency, (2) cheap, nontoxic and efficient fluorescent agents can be applied in low concentrations onto spills by conventional crop-dusting or spray techniques, and (3) underwater sonic sensing provides excellent synergistic effects with the fluorescence technique.

Francis T. Mayo, Director
Municipal Environmental Research Laboratory

ABSTRACT

Three new techniques were investigated for controlling and recovering oil and floating hazardous material spills in water bodies: amine carbamate gelling agents, fluorescent agents for night-time operations, and environmental sonic sensing. These methods are aimed at solving the serious problems posed by the poor visibility that often accompanies spill situations. Operational capability is nonexistent at night or during other periods of low visibility. But fast, continuous action is essential to recovery operations, since cleared areas can be covered again in just a few hours as the unharvested contaminant drifts back over the cleared track. Moreover, skimmer operations are most efficient with thicker pollutant films. Thus the spreading of the material both increases the operational area and decreases cleanup efficiency.

Amine carbamate gelling agents can be used to gel spills quickly and completely to a solid consistency. This gel is much more visible than oil, (for example) does not readily flow or spread, is very easily, quickly, and completely recovered by nets or sieves, is much less volatile (and thus less hazardous with regard to fire and toxicity), does not permeate sand or other porous materials, and can be easily regenerated into the original HM and gelling components.

Cheap, nontoxic, and highly efficient fluorescent agents can be applied in low (50 ppm) concentrations onto spill areas by conventional crop dusting or spraying techniques. In open water with no pollutant cover, the fluorescer is dissipated into the water column; but it is preferentially retained without extraction into the water wherever there are pollutant patches. At night, commercial UV (ultraviolet or "black" light) display lights (or modified ordinary mercury vapor street lights) can be beamed over the spill area. Vivid fluorescent illumination occurs only from spill patches, thereby making such areas easily visible and extending spill control and recovery operations into night-time hours.

Underwater sonic sensing techniques were shown to be excellent means of locating near-surface pollutant. In typical spill situations, a large portion of the pollutant is in a floating globule near the water surface as a result of surface wave action. This condition is particularly common for high-density materials. Sonic sensing can also provide much-needed information on the rate of dissipation of pollutant into the water column. Sonic sensing and fluorescent techniques also have excellent synergistic capabilities when used together, though both techniques are excellent alone.

This report was submitted in fulfillment of Grant Nos. R804628-0 and R806118-01 under the partial sponsorship of the U.S. Environmental Protection Agency. The report covers the period September 15, 1978, to September 14, 1979, and work was completed as of May 15, 1982.

CONTENTS

| | |
|---|-----|
| Forward | iii |
| Abstract | iv |
| Figures | vii |
| Abbreviations and Symbols | x |
| Conversion Factors | xi |
| Acknowledgements | xii |
| 1. Introduction | 1 |
| 2. Conclusions | 5 |
| 3. Recommendations | 10 |
| 4. Results | 11 |
| Preliminary U.S. Navy Oil Spill Study. | 11 |
| OHMSETT Test I: Extrapolation of Amine Carbamate System to Large-Scale Situation | 22 |
| Bay "F" Test I: Carbamation by Liquid/ Gaseous CO ₂ Systems | 29 |
| OHMSETT Test II: Design, Construction and Testing of Prototype Spill Control and Recovery Equipment | 33 |
| Bay "F" Test II: Design, Construction and Testing of Prototype Portable Spill Control and Recovery Equipment | 34 |
| Field Tests at U.S. Naval Submarine Base, New London, Connecticut | 44 |
| Use of Fluorescent Agents and Acoustic Sensing for Night-Time Spill Recovery and Control Operations | 59 |
| References | 73 |
| Appendices | |
| A. Amine D(TM) and its Derivatives, Bulletin OR-132C, Hercules, Incorporated | 75 |
| B. Toxicity of Hercules Amine D to Marine Life | 83 |
| C. Toxicology Data Sheets, Uvitex OB and Nopol | 94 |
| D. Volatility and Flash Point Studies | 99 |
| E. Submissions of Product Listings for Inclusion in Survey of Equipment for Oil and Floating Hazardous Material Spill Countermeasures | 101 |
| F. Near-Surface Water Column Profiling by Acoustic Sensing as a Complementary Means to Define Extents of Low-Visibility Oil and Hazardous Chemical Spills | 112 |
| G. Report of Oil Spill Control and Recovery Field Tests at U.S. Naval Submarine Base, New London, Connecticut | 121 |

| | | |
|----|--|-----|
| H. | Fluorescent Agents for Night-Time Operations: Results of Tests Aboard EPA OSV Antelope, 14 September 1981 . . | 123 |
| I. | Proposed Oil and Hazardous Chemical Spill Control and Recovery by Amine Carbamate Gelation | 130 |
| J. | Proposed Use of Fluorescent Agents and Acoustic Sensing for Night-Time Spill Recovery and Control Operations | 137 |

FIGURES

| <u>Number</u> | <u>Page</u> |
|---|-------------|
| 1 Amine D sprayer | 14 |
| 2 Application of dry ice | 15 |
| 3 Gelation occurs quickly | 16 |
| 4 Harvesting gelled oil | 17 |
| 5 Detail of gelled oil | 18 |
| 6 Recovery operation using DIP skimmer craft | 19 |
| 7 Another view of DIP skimmer | 20 |
| 8 Herding of gelled oil using Navy piston film | 21 |
| 9 Pump for delivery of Amine D solution to sprayers | 23 |
| 10 OHMSETT sprayers in action | 24 |
| 11 Surface breaker equipment | 25 |
| 12 Application of powdered dry ice | 26 |
| 13 Recovery of gelled oil by means of nets | 27 |
| 14 Sand permeability of gelled versus ungelled oil | 28 |
| 15 Spraying operation at Bay "F" Test I | 30 |
| 16 Carbonation at Bay "F" Test I | 31 |
| 17 Recovery of gelled oil by means of sieve | 32 |
| 18 "Compass Rose" underway in OHMSETT tank | 35 |
| 19 Spraying apparatus on "Compass Rose" | 36 |
| 20 Carbonation from "Compass Rose" | 37 |
| 21 Gelled oil in OHMSETT tank | 38 |

FIGURES (continued)

| <u>Number</u> | | <u>Page</u> |
|---------------|---|-------------|
| 22 | Gelled oil in OHMSETT tank | 39 |
| 23 | Recovery of gelled oil by net | 40 |
| 24 | Portable hand-operated filter press | 41 |
| 25 | Filter press in operation | 42 |
| 26 | Wave action effects on "Compass Rose" intakes | 43 |
| 27 | Spraying apparatus in operation at Bay "F" Test II | 45 |
| 28 | Carbonation apparatus at Bay "F" Test II | 46 |
| 29 | Gelled oil at Bay "F" Test II | 47 |
| 30 | Herding of gelled oil with screen | 48 |
| 31 | Gelled oil at Bay "F" Test II | 49 |
| 32 | Recovery of gelled oil by net | 50 |
| 33 | Loading rubber raft assembly at New London Sub Base | 51 |
| 34 | Filling Amine D canisters on raft | 52 |
| 35 | Rubber raft equipped at submarine base | 53 |
| 36 | Rubber raft manned, awaiting boom placement | 54 |
| 37 | Raft "Titanic" in operation at submarine base | 55 |
| 38 | Another view of raft operation | 56 |
| 39 | Trimaran craft at submarine base | 57 |
| 40 | Gelled oil from stern of trimaran raft | 58 |
| 41 | Use of fluorescent agents and acoustic sensing for night-time oil spill recovery and control operations | 60 |
| 42 | Compatibility of chemicals with fluorescence and sonic sensing techniques | 61 |
| 43 | Commencement of fluorescence test | 63 |
| 44 | Results of fluorescence test | 64 |

FIGURES (continued)

| <u>Number</u> | <u>Page</u> |
|--|-------------|
| 45 EDO Aero 14B airborne spray tank (and auxiliary equipment). . . | 65 |
| 46 Another view of EDO spray tank | 66 |
| 47 Commencement of fluorescence dusting test | 67 |
| 48 Dusting with fluorescent powder | 68 |
| 49 Results of fluorescence test | 69 |
| 50 Cropdusting by helicopter | 70 |
| 51 Breakup of ARGO MERCHANT | 71 |
| 52 Oil slick from ARGO MERCHANT | 71 |
| 53 EPA ocean survey vessel ANTELOPE | 72 |

ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

| | |
|-----------|---|
| Amine D | -- dehydroabietylamine (or, 1,4a-dimethyl-7-isopropyl 1,2,3,4,4a,9,10,10a-octahydro-1-phenanthrenemethylamine) |
| cm | -- centimeter |
| DC | -- direct current |
| DIP | -- dynamic inclined plane |
| hp | -- horsepower |
| hr | -- hour |
| kg | -- kilogram |
| lb | -- pounds |
| m | -- meter |
| ml | -- milliliter |
| Nopol | -- 6,6-dimethylbicyclo[3.1.1.]hept-2-ene-2-ethanol |
| NRL | -- Naval Research Laboratories |
| OHMSETT | -- Oil and Hazardous Materials Simulated Environmental Testing Tank |
| Pa | -- Pascal |
| psi | -- pounds per square inch |
| PVC | -- polyvinyl chloride |
| rpm | -- revolutions per minute |
| UV | -- ultraviolet light |
| Uvitex OB | -- trade name (Ciba-Geigy Corp.) for a proprietary stilbene fluorescer |
| V | -- volts |

SYMBOLS

| | |
|----|-----------------------|
| °F | -- degrees Fahrenheit |
| °K | -- degrees Kelvin |
| ' | -- foot |
| " | -- inch |

CONVERSION FACTORS

Inasmuch as all equipment that was constructed for the current project and that is proposed for future work has and will be designed in accordance with English units, all units of measurement in this report will generally be in English units.

| | | | |
|---------|----|----------------|---|
| °F | to | °K | subtract 32, multiply by 0.555, and add 273 |
| feet | to | meters (m) | multiply by 0.3048 |
| gallons | to | m ³ | multiply by 3.785×10^{-3} |
| hp | to | watts | multiply by 746 |
| inches | to | meters | multiply by 0.0254 |
| knots | to | m/hr | multiply by 1,852 |
| lbs | to | kg | multiply by 0.454 |
| psi | to | Pascals (Pa) | multiply by 6.895×10^3 |

ACKNOWLEDGMENTS

Major support for the various phases of the research as discussed in this report was provided by the U.S. Environmental Protection Agency and the U.S. Navy. We are also grateful to the Cardox Division of Chemetron, Inc.; the Ciba-Geigy Corp.; Flexcon Corp.; GTE Laboratories, Inc.; the Hercules Corp.; Morton Chemical Co.; Norda, Inc.; and the Shell Oil Company for generous donations of funds, equipment, and technical information in support of the project work. The University of Lowell Alumni Association provided research fellowships for several of the students working on this project, which was much appreciated by the group.

Mr. Uwe Frank of the Edison, New Jersey, Municipal Environmental Research Laboratory of the EPA, and Dr. William Garrett of the Naval Research Laboratories were project officers for most of the work reported herein. Their suggestions and technical expertise were vitally important to the success of the overall project operations.

Grateful acknowledgement is extended to Captain Dwight Paine and the crew members of the EPA Ocean Survey Vessel ANTELOPE, which was provided to us for the very successful sea test involving use of fluorescent agents for night-time spill operations. Mr. Edward S. McLean of the EPA and Mr. Robert Blase and Dr. Leslie Pierre of the MAR Corporation (operators of the ANTELOPE) were helpful to us in making the ship available and in providing valuable technical assistance and advice prior to and during these tests.

The assistance and cooperation provided by the Mason & Hanger - Silas Mason Company's OHMSETT facility, and by the Commanding Officer and crew of the Naval Submarine Support Facility at New London, Connecticut, were also invaluable to our group in the course of our project work at their facilities.

We also wish to acknowledge the considerable assistance provided to us by the following individuals: Mr. Cesar Aguilar, President, SEA International; Mr. Ralph Bianchi, President, JBF Co.; Mr. Robert Castellucci of the Naval Facilities Engineering Command, and Chief David Miller, USN; Mr. Donald Sounia of the Cardox Company; Mr. George Duggan, Mr. Robert Edelson, and Mr. Joel Finkel of GTE Labs/Sylvania Corp.; and Mr. John Farlow and Mr. Leo McCarthy of the EPA's Edison Laboratories.

Finally, we wish to thank the students (numbering more than 60) of this group whose ideas, enthusiasm, and industry made all the results of the group possible. We also wish to dedicate this report to the memory of the late Dr. Howard Reynolds, Chairman of the Chemical Engineering Department, who helped to conceive the ideas underlying this project.

SECTION 1

INTRODUCTION

In recovery operations for oil and hazardous material* slicks on water surfaces, a number of devices and techniques have been devised and implemented. Destructive procedures include removal by burning; sorption into straw or other material to facilitate oil removal for subsequent destruction, or into chemically treated sand or other agents that cause the oil to sink; microbial agents that digest the oil; and dispersion with surface-active agents that tend to break up the oil slick to facilitate solution and eventual microbial degradation (1). Nondestructive devices and techniques include the use of polymeric sorbents that can be spread over a slick to absorb the oil, with subsequent recovery of the oil by squeezing from the sorbent; passive restraint systems such as booms, which prevent further spread of a slick; and active systems such as oil skimmers, which remove oil by a variety of techniques, from the surface of the water by mechanical action (2).

Disadvantages of destructive techniques include loss of the oil and the very serious negative environmental impact on the water and/or atmosphere. Serious problems are also associated with nondestructive recovery attempts. Under the most ideal conditions, it is usually not feasible to recover much more than 90% of a given spill. Recovery efforts are slow and often frustrating; most oil skimmers, for example, have a maximum operational speed of 3 knots. Oil slicks usually move back over the previously cleared track made by a skimmer, so little progress can be made in terms of actual complete clearing of a given area. Because of the slick's slow operational speed, the actions of wind, current, and the migrational tendency of the oil slick can all change the contour and overall area of the slick at the same time the skimmer is attempting its recovery effort.

Oil slicks are often difficult to distinguish from open water areas, particularly at low elevations from the surface of the water. Thus the helmsman of a skimmer craft may find it extremely difficult to follow a proper track in the recovery of an oil slick. Visibility of oil slicks is particularly low at dusk or in other periods of poor light.

* The terms "oil and "hazardous material" are frequently used interchangeably in this report. Gelation, fluorescence, and sonic sensing techniques are applicable (except where otherwise noted) to all organic hazardous chemical and oil spills.

Additives have been introduced from time to time to facilitate collection of oil slicks by gelation or other agglomerative processes involving the oil. These agents are often expensive, and problems invariably arise in the addition of the agent to the oil (viscous interfaces between the oil and the gelling agent tend to prevent complete and rapid distribution), and frequently in the separation of the oil from the gel in recovery operations (3).

Recovery work performed by the EPA (4) indicates that the following observations generally hold for conventional gelling agents or similar additives:

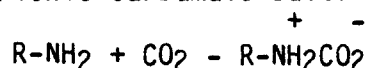
1. Introduction of congealing agents into hazardous material spills enables a stable boom to contain the material at a higher current velocity or tow speed in calm water.
2. To optimize the effect of such agents, time for mixing and absorption must be allowed, depending on wave condition and turbulence.*
3. Because of splash-over failure, such agents do not enhance containment in the presence of 0.3-meter harbor chop.
4. Agent acquisition, transportation, distribution, separation, recycling, and disposal substantially increase the time required for cleanup efforts.*
5. In some instances, the use of such agents may permit a higher recovery craft speed than would be the case if such agents were not used.
6. Vapor concentrations above systems involving sorbents (not gelants) were sometimes actually higher than when sorbents were not used.*
7. Use of sorbents substantially reduces the extent of emulsification of hazardous material into the water column.*

Our research group became quite active some time ago on processes (5) whereby hydrocarbon and other organic liquid formulations would be gelled to a solid consistency quickly, safely, and economically, using readily available amines. These can be easily admixed with oils to form a complete solution before gelation occurs, thus completely avoiding any possibility

* As will be noted in appropriate sections of this report, the limitations noted in items 2, 4, and 6 were not as serious in the observations made in this investigation of amine carbamate gelling agents. Thus very little or no mixing time is required; the greatly increased speed and efficiency of collection greatly offsets the other increased time requirements and there appears to be a greatly reduced (not increased) vapor concentration over amine carbamate gelled systems.

of the formation of viscous interfaces between the oil and the gelling agent.

This process depends on the action of carbon dioxide on a primary amine to form a zwitterionic carbamate salt:



(If an aqueous system is present and a desire exists to prevent solution of the carbamate in the water, a high-molecular-weight primary aliphatic or alicyclic amine is chosen, with attendant low water solubility.) The amine is oil soluble, and a thorough solution is easily and quickly attained, whereupon carbon dioxide can be added for rapid gel formation (usually within a few minutes). Moreover, oil or other organic formulations can be separated rather easily and quickly from the gelled mixture by filter pressing, centrifuging, or a variety of chemical techniques. And in all such instances the amine gellant could be regenerated very economically for subsequent reuse.

Thus it appears that the principal disadvantages inherent in previously studied gelling systems do not apply to the amine carbamate system in terms of potential use in oil spill recovery efforts.

Since 1976, our group has been working on the use of this and related processes for oil and hazardous material spill recovery and control operations.

These other developments are largely related to the very serious problems of poor visibility associated with typical oil and hazardous chemical spill situations. No operational capability exists at night or in other periods of low visibility, when operating personnel are unable to discern spill boundaries. But time is extremely important in spill control and recovery work; in a few hours, areas cleared of a spill by skimming or similar operations can be covered again as unharvested oil or chemicals drift back over the cleared track. Moreover, skimmers are most efficient with thicker films. Thus spreading the oil not only increases the operational area, but also decreases film thicknesses with an attendant decrease in efficiency.

In our earlier work we demonstrated that commercially available, nontoxic and highly efficient fluorescent agents with both oil and water compatibility could be applied in very low concentrations to oil spills with excellent results. At night, when natural light is sufficiently diminished to permit visibility of fluorescent light, UV light could be beamed over the spill area to illuminate the resulting fluorescence from the oil spill patches. The perimeters of such areas would thus be easily discerned, and operational capabilities would be extended into night-time hours. This procedure could be particularly important in situations occurring in winter months in higher latitudes, when night-time conditions are significantly prolonged.

At about the same time, information began to become available regarding new developments in underwater environmental acoustic sensing techniques, whereby sophisticated sonar gear can be used to detect dispersions of organic material into near-surface areas of large bodies of water.

Thus, as work progressed in oil and hazardous chemical spill recovery, it became of increasing interest to investigate the possibilities of synergistic results that might accrue on combination of two or more of the gelation, fluorescence, and sonic sensing processes.

The overall project work to be described in this report will be discussed in the following order of development:

1. Preliminary investigations (sponsored by the U.S. Navy, 1975-1976).
2. ~~OHMSETT Test I:~~ Preliminary extrapolation to larger scale situations (EPA, ~~1976~~ 1977).
3. Bay "F" Test I: Carbamation by Liquid/Gaseous CO₂ Systems (EPA, early 1978).
4. OHMSETT Test II: Design, Construction and Testing of Prototype Hazardous Material Spill Control and Recovery Equipment (EPA, 1978).
5. Bay "F" Test II: Design, Construction and Testing of Prototype Portable Spill and Recovery Equipment (EPA, 1979).
6. Field tests at U.S. Naval Submarine Base, New London, Connecticut (U.S. Navy, 1980-1981).
7. Use of Fluorescent Agents and Acoustic Sensing for Night-Time Oil Spill Recovery and Control Operations (EPA; GTE Laboratories, Inc., 1981-present).

SECTION 2

CONCLUSIONS

The following conclusions pertain to the work performed on this project, and are presented in the order discussed in Section 4 (Results) of the report.

PRELIMINARY U.S. NAVY OIL SPILL STUDY

1. The optimum gelling agent is comprised of a mixture of 70% Amine D, 15% ethyl alcohol, and 15% Nopol, applied in a concentration of approximately 15% in the oil or hazardous chemical spill.
2. The solubility of Amine D in water is very low--less than 1 part per million. Only with extreme agitation will any degree of emulsification in water occur. For ordinary wave action in open water, there would probably be no emulsification problem; pounding coastal surf might cause emulsification, probably of the same order of magnitude as is the case with oil in such surf.
3. Toxicities of the components of the gelling agent formulation are low, of the same order of magnitude (or less) than that of hydrocarbon oil.
4. Film thickness of the oil or hazardous chemical spill does not appear to be a factor in terms of efficiency of gelation.
5. The optimum carbamating agent has proven to be liquid or gaseous carbon dioxide.
6. The optimum method of separation of gelled oil or hazardous chemicals into the original ungelled material and the gelling agents is pressure filtration. Yields of more than 90% of the original oil can be recovered, with essentially no contamination by either Amine D or Nopol. The filter cake contains the remaining oil, the amine carbamate, and the Nopol. The amine carbamate can be heated to 100°C to reverse the carbonation process, affording Amine D and Nopol which can then be reused for subsequent gelation work.
7. Very significant reductions in rates of volatilization result on amine carbamate gelation of organic chemicals, by as much as 50%. Flash points of flammable materials are correspondingly increased, with resulting decreases in fire hazards; toxicity hazards are also correspondingly decreased.

8. Many hazardous chemicals other than hydrocarbons are easily gelled by this system. Not all organic compounds are easily gelled, however. Important exceptions include: extremely thick and viscous materials, in which solution of the amine solution is difficult to achieve readily; acidic compounds (which react with the basic amine) do not gel; unsaturated vegetable oils form gels of rather weak mechanical strength, as is the case of some high-molecular-weight naphthenic hydrocarbons as are often found in lubricants. The large majority of organic compounds do form satisfactory gels, however. In the event the nature of a hazardous material spill is not known, a simple and quick test can be performed on a small (approximately 25-ml) sample of the material by adding about 15% of the gelling agent and treating with carbonated water.
9. Beach-front protection is afforded by gelation of incoming spills; ungelled materials readily soak into sand, whereas gelled materials do not, thereby very considerably facilitating beach cleanup efforts.
10. Very significant advantages can be realized in use of amine carbamate gelation processes. The gelled oil or hazardous chemical spill is immobilized and will not readily move back over a cleared track (as will ungelled spills); the ease and speed of recovery is very greatly increased, as is the extent of recovery; the gelled spill is of much higher visibility than ungelled liquid spills; nets, sieves, and similar retrieval equipment provide excellent recovery results (these being totally useless with liquid spills); storage and transport of gelled recovered spills presents no destabilizing free surface effects (i.e., "sloshing") in recovery craft or barges; unconventional containers such as burlap or plastic bags, cardboard boxes and the like can be used for short-term storage of gelled recovered spill material (these being totally unsuitable for ungelled material), and the ability to use such containers in any available deck space permits the use of any kind of vessel for such recovery work (whereas liquid spill recovery vessels must have special liquid cargo holds or tanks).

OHMSETT TEST I: EXTRAPOLATION OF AMINE CARBAMATE SYSTEM TO LARGE-SCALE SITUATIONS

1. This series of tests confirmed the feasibility of use of the amine carbamate gelation system in relatively large situations.
2. The use of solid dry ice as a source of carbon dioxide was shown to be very infeasible, due to procurement, transportation, storage, and cost considerations. Also, dry ice is affected adversely by rain or high humidity.

BAY "F" TEST I: CARBAMATION BY LIQUID/GASEOUS CO₂ SYSTEMS

1. In this test it was shown that commercially available liquid CO₂ in cylinders or tanks delivered in liquid or gas form was an optimum carbamating agent with none of the drawbacks associated with solid dry ice.

2. Improved Amine D sprayer systems were designed and constructed, as were CO₂ bubbler systems.
3. It became apparent that a two-pass system (with separate phases involving application of Amine D as a spray, followed by a subsequent pass with application of CO₂) would be infeasible in field operations.

OHMSETT TEST II: DESIGN, CONSTRUCTION, AND TESTING OF PROTOTYPE HAZARDOUS MATERIAL SPILL CONTROL AND RECOVERY EQUIPMENT

The main objectives of this test series were the design, construction, and testing of a control and recovery craft that would effect gelation of an oil spill by simultaneous spraying and carbonation of the slick in a single pass. It was concluded from this series of tests that:

1. Large spill areas (an acre or more) could be treated and controlled quickly (within 10 minutes) by use of a craft that could contain reasonable quantities of gelling agents (i.e., 400 gallons of Amine D solution and 750 pounds of carbon dioxide). Complete recovery of the resulting gelled oil could be effected in about the same time interval by means of followup craft equipped with suitable netting gear.
2. For other than smooth water surfaces (e.g., in harbor chop conditions), further attention needed to be given to design of the sprayer/carbonator assemblies. Specifically, the interaction of confused seas with the bow wave of conventional harbor craft tends to force a large amount of oil in the intended track of the craft to either side and away from the reach of the sprayer/carbonator assemblies mounted on such craft. To avoid this, one solution would be to mount these assemblies further forward and further outboard of the craft.
3. Although such a craft would be useful in harbor work, or in similar areas where storage and maintenance of the craft would present little problem, a need could exist for a portable spill and recovery craft that could be easily assembled and disassembled, and that could be easily stored and transported from central locations to remote spill areas.

BAY "F" TEST II: DESIGN, CONSTRUCTION, AND TESTING OF PROTOTYPE PORTABLE SPILL CONTROL AND RECOVERY EQUIPMENT

In this test a small three-man rubber raft was modified to provide a small-area spill control and recovery craft that could easily be stored and transported to remote spill sites. In the small confines of the Bay "F" test pool, excellent results were obtained, suggesting that the craft would be of use in possible remote spill situations, particularly in inland waters with little or no wave action.

FIELD TESTS AT U.S. NAVAL SUBMARINE BASE, NEW LONDON, CONNECTICUT

Several tests were performed at this activity in late 1980 and early 1981, in attempts to reduce to practice, in actual oil spill situations, the concepts and techniques that had been developed in the previous test programs. The following conclusions were derived:

1. The small rubber raft developed in the Bay "F" exercise was found to be totally unsuitable for open water work, particularly as it was modified in this work to enable a dual capability for spraying and carbonating in one pass. The raft was so overladen with equipment that it presented danger of swamping even in small waves of less than 2 feet in the open water.
2. The raft was considered safe and feasible to use under "mill pond" conditions as could be encountered in small lakes or other small bodies of water with spill situations. It was considered advisable, even for these calm condition situations, to have a more sturdy craft with higher freeboard and greater stability. A further advantage would also derive from having increased capabilities for larger spills, in terms of the larger gelling agent loads such a larger craft could carry.
3. In subsequent tests at the Submarine Base, a trimaran (three-hulled raft) was utilized, with excellent results. This craft was quite stable in wave conditions up to 2 feet. It is quite sturdy, and can easily carry up to 2.5 tons of equipment and supplies, in addition to a crew of five technicians. It is capable of being powered to attain working speeds of up to 5 knots, which would enable coverage of up to an acre of oil slick area to be controlled in approximately 10 minutes, using gelling equipment and supplies that can be carried on the trimaran. By installation of appropriate intake booms at the bow of the trimaran, bow wave problems (i.e., the tendency for interaction of the bow wave with confused seas to cause sweeping of incoming oil to be swept to either side of the craft) should largely be eliminated.
4. Further work would be desirable to develop a portable trimaran that could be easily assembled, disassembled, capable of being stored and transported with all required equipment and supplies in a small van, and capable of gelling and controlling a large spill area quickly and completely. The use of nets towed behind the craft could enable simultaneous control and recovery of such spills.

USE OF FLUORESCENT AGENTS AND ACOUSTIC SENSING FOR NIGHT-TIME HAZARDOUS CHEMICAL SPILL RECOVERY AND CONTROL OPERATIONS

A number of small tests had been performed, commencing as early as the preliminary U.S. Navy Oil Spill Studies of this overall series, in which it was demonstrated that use of fluorescent agents when applied to oil or hazardous chemical spills would provide excellent night-time operational capabilities. Full-scale research efforts in this direction were instituted in mid-

1981, with extension also to sonic sensing techniques in the Fall. The following observations and conclusions pertain to this on-going work.

1. Fluorescent agents can be applied in the form of sprays of liquid solutions of such agents, or by dusting with powder formulations. Current tests strongly indicate that the dusting operation is the more feasible, although both techniques have proven to be extremely promising.
2. Concentrations of fluorester in oil spills are quite effective for excellent night-time visibility, when applied as low as 59 parts per million in the oil.
3. The best dust formulation appears to be an intimate mixture of the fluorester in powdered gypsum (CaSO_4). The optimum spray formulation appears to be a solution of the fluorester in di- or tripropylene glycol monomethyl ether solvents.
4. Uvitex OB(TM) (Ciba-Geigy Corp.) and Yellow 131SC(TM) Morton Chemical Co.) have proven to be excellent nontoxic, cheap, and highly effective fluorescers.
5. The gypsum powder base is entirely nontoxic and with no fire or other hazardous character associated with use. Glycol ether solvents have very low fire and toxicity hazards, and in the concentrations contemplated for use would probably present no significant hazard.
6. Underwater sonic sensing techniques were shown to have excellent synergistic effects when used with the fluorescent techniques. Both techniques would be excellent when used on a stand-alone basis. Sonic sensing is particularly invaluable in situations in which a need exists to determine the rate of dissipation of oil into the water column.

SECTION 3

RECOMMENDATIONS

In view of the successful results of the research performed in the course of the EPA, Navy, and similar projects discussed in this report, further work is proposed to extrapolate these results to full-scale operational situations, with construction, testing, evaluation, and full utilization of appropriate equipment and procedures.

The proposed work would have the following objectives:

1. Design, construction, testing, and utilization of a prototype trimaran craft for use in hazardous chemical spill recovery and control operations in inland waters and in harbor situations. The craft will be portable, easy to assemble and disassemble, capable of supporting a load of approximately 12,000 pounds for recovery and control operations over an area of about an acre in about 5 minutes, gelling up to 2,200 gallons of spilled chemicals in a track up to 17 feet in width and 1/2 mile in length. Equipment for operations with fluorescent agents under night-time conditions will be available. The craft, when disassembled, would be stored and transported in a truck-trailer space of about 8 by 12 by 6 feet, along with all required chemicals and supplies.

Reference is made to Appendix I of this report for detailed discussions and specifications for the proposed trimaran craft and for its operation.

2. Performance of full-scale tests with application of fluorescer from aircraft or from ships onto oil or hazardous chemical spills in wide open water situations, with subsequent illumination at night by UV floodlights, to permit full-scale night-time recovery and control operations. Acoustic sensing gear operated from recovery vessels will be utilized to permit auxiliary reconnaissance in terms of locating and tracking such spills, and in ascertaining the course of recovery and control work.

Reference is made to Appendix J of this report for detailed discussions of the salient features of the proposed tests.

SECTION 4

RESULTS

Results of the work performed on this overall project are discussed in the chronological order of the undertaking of the major phases of the project:

1. Preliminary U.S. Navy Oil Spill Study
2. OHMSETT Test I: Extrapolation of Amine Carbamate System to Large-Scale Situations
3. Bay "F" Test I: Carbamation by Liquid/Gaseous CO₂ Systems
4. OHMSETT Test II: Design, Construction and Testing of Prototype Hazardous Material Spill Control and Recovery Equipment
5. Bay "F" Test II: Design, Construction and Testing of Prototype Portable Spill and Recovery Equipment
6. Field Tests at U.S. Naval Submarine Base, New London, Connecticut
7. Use of Fluorescent Agents and Acoustic Sensing for Night-Time Oil Spill Recovery and Control Operations

PRELIMINARY U.S. NAVY OIL SPILL STUDY

In the early part of this phase of the project work, there was undertaken a study of the physical properties of these gel systems, including the following topics:

1. Optimization of gelling agent. Of more than 60 commercially available, low-toxicity, water-insoluble amines studied, dehydroabietylamine ("Amine D") was by far the most effective as a gelling agent for oil and hazardous chemical spills on water surfaces. The optimum formulation was found to be comprised of 70% Amine D, 15% ethyl alcohol, and 15% 6,6-dimethylbicyclo-(3.1.1)-2-heptene-2-ethanol ("Nopol").
2. In determining the solubility of Amine D as the CO₂ carbamate salt in water, both fresh and salt water samples were saturated by shaking with Amine D carbamate for 15 minutes. Using techniques described by Ghosh and Whitehouse (7), NBD Chloride (7-chloro-4-nitrobenzo-2-oxa-1,3-diazole) was used as a fluorogenic reagent with

both aqueous systems and with standard alcohol solutions of Amine D. By comparison of the fluorescence spectra, it was determined that the solubility of Amine D in water was less than 1 part per million; work done at the EPA in Edison, New Jersey, with different fluorogenic reagents confirmed these findings (8).

3. In determining the emulsification tendency of standard gels formed by action of Amine D on No. 2 fuel oil in water, no significant emulsification occurred in test flasks at stirrer speeds up to 250 rpm over time intervals of 5 minutes. Some emulsification, unstable to the extent that phase separation occurred within 10 minutes, took place at stirrer speeds around 1000 rpm. With blender stirrer speeds up to 20,000 rpm, complete emulsification occurred with no phase separation within 1 day. From results of this work, and from observation of tests performed at OHMSETT facilities with imposed wave actions up to 1.1 meter harbor chop conditions (in which no observable emulsification occurred), it can be concluded that for most sea conditions in open water, no problem should be anticipated in terms of emulsification or other means of dispersion into the water. Dispersion and emulsification might be a problem in the case of heavy pounding surf.
4. Investigations were undertaken in determining the optimum carbamating agent. Metal and ammonium carbonates and bicarbonates, and ammonium carbamate all had varying efficiencies as CO₂ sources, but none of these were judged to be as effective or desirable from any standpoint as liquid, solid, or gaseous CO₂ itself. Unsuccessful attempts were made to find a solvent cheap enough, water-soluble, and nontoxic for use with precarbamated amine, which it was hoped could thereby be sprayed directly into an oil or hazardous chemical spill to afford gelation without a need for followup with a CO₂ treatment after spraying the amine onto the spill.
5. Attempts were made to optimize the capability of separating gelled oil into the oil and amine carbamate components, the former for immediate availability for use in its intended application, and the carbamate for reconversion to the amine for subsequent reuse in spill control and recovery operations.

Centrifuging represents one such method of separation, but the requirements for adequate separation probably amount to an overall infeasibility for real-life field situations. Separations of up to 60% of the original oil were achieved using centrifuge speeds of 4,500 rpm, with centrifuging forces over 2,500 g in a time interval of 15 minutes.

Extraction of oil from the gel after conversion of the amine to the hydrogen sulfate (by treatment with dilute sulfuric acid) also proved infeasible. Even after prolonged water washing of the oil phase residual levels of the amine salt were still contained in the oil.

Filter pressing proved to be an effective means of separating components of the gel. With ordinary vacuum filtration (less than 1 atm

of pressure on the filter cake) in a Buchner funnel with rubber dam covering the cake, separations in excess of 80% of the original oil were readily achieved. Using fluorescence spectroscopy with NBD Chloride as previously described (7), less than 1 part per million of Amine D was detected in the oil phase; by gas chromatography, no Nopol was found in the oil phase. The resulting filter cake contained about 18% of the original oil and essentially all the Amine D and Nopol. Higher filter pressures should be even more effective.

6. Toxicity levels, with regard to marine life, were conducted in this phase of the project work; cf. the report of the Lahey Clinic Sias Laboratories, Appendix B to this report. In summarizing this work, it was found tht suspensions (not true solutions) of up to 20 ppm of Amine D in sea water posed no greater toxicity effects to marine life than would be encountered with similar levels of fuel oil (or similar hydrocarbon compositions). Inasmuch as Amine D has a solubility of less than 1 ppm, and since introduction of the amine into the water column is not an efficient process by emulsification or similar dispersion mechanism, it would appear that the use of Amine D as a gelling agent in spill control and recovery operations would pose no serious threat to marine life, and no more so than is posed by oil spills per se. In terms of the facilitation of the recovery and control of the spill, there is an obvious reduction of toxic effects to marine life provided by use of this system in such spill control and recovery efforts.

As is described in Appendices A and B to this report, Amine D is not only of low toxicity, but also is not a significant skin sensitizer. Throughout the 7 years in which this compound has been tested in oil spill control and recovery work by more than 50 members of this research group, three minor skin rashes were observed by three individuals. On each of these occasions these individuals had been working with other compounds or formulations (in one instance, toluene; on the other two occasions, No. 2 fuel oil), in large quantities of up to 50 gallons. It is deemed as likely that these rashes (which disappeared in less than 1 day) were due to other compounds as that they were due to Amine D. These same individuals were exposed to Amine D on numerous other occasions with no untoward effects. Although care should be exercised in working with Amine D, as would be the case with any other chemical agent, this compound appears to be safe.

Preliminary tests were undertaken in the Summer of 1977 at the JBF Company at Wilmington, Massachusetts, in small-scale field testing of the amine carbamate system for use in oil spill control and recovery. Amine solution sprayers, dry ice spreaders, and recovery nets and sieves as had been developed were tested, as was the use of DIP (Dynamic Inclined Plane) skimmer craft, and capabilities for storage of gelled oil in makeshift containers such as plastic bags and cardboard boxes were investigated. The results of these tests are shown and discussed in Figures 1 through 8. Extremely efficient recoveries (more than 99% oil recovery), greatly enhanced visibility of gelled oil versus ungelled oil, and excellent compatibility of the system with use of



Figure 1. Amine D sprayer.

A 3-gallon garden spray can is being loaded with 2.5 gallons of 70% Amine D/15% Nopol/15% ethyl alcohol. The sprayer is pressurized by a hand pump that screws into the top.

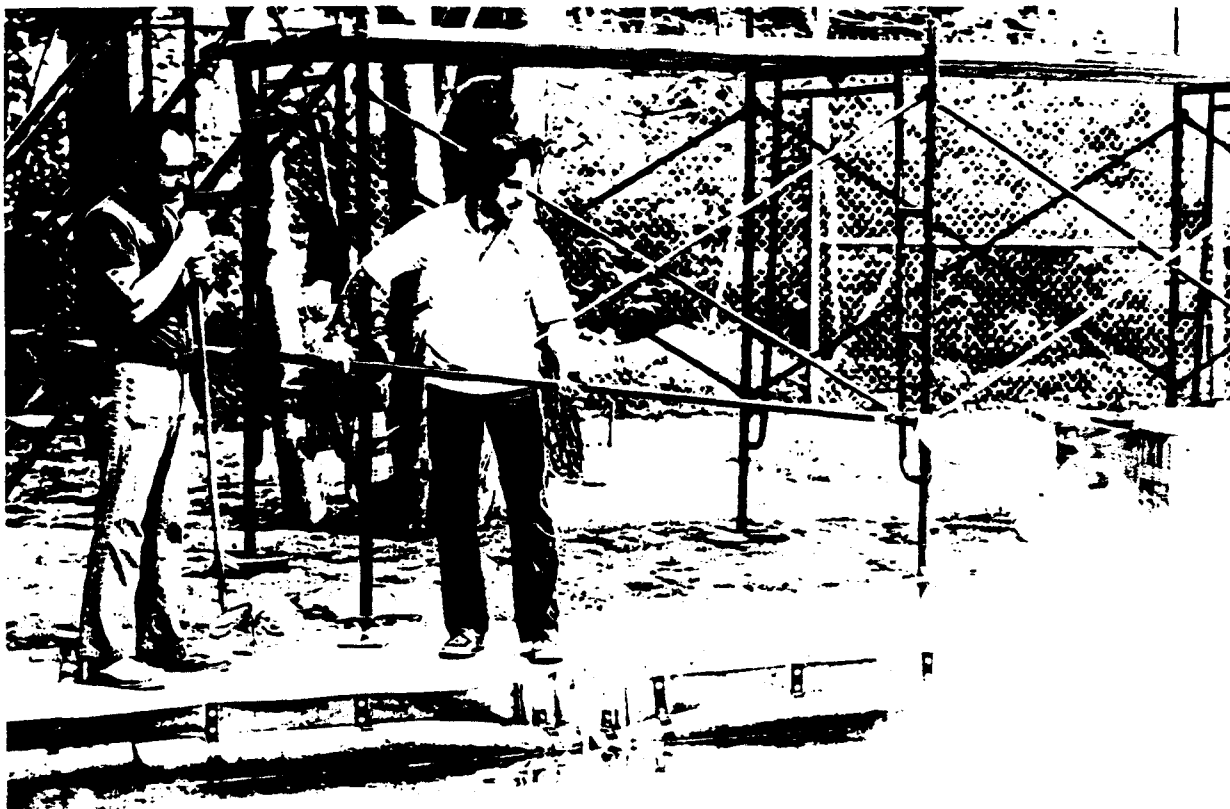


Figure 2. Application of dry ice.

Five pounds of crushed dry ice is applied to oil slick/Amine D solution using sieving technique.

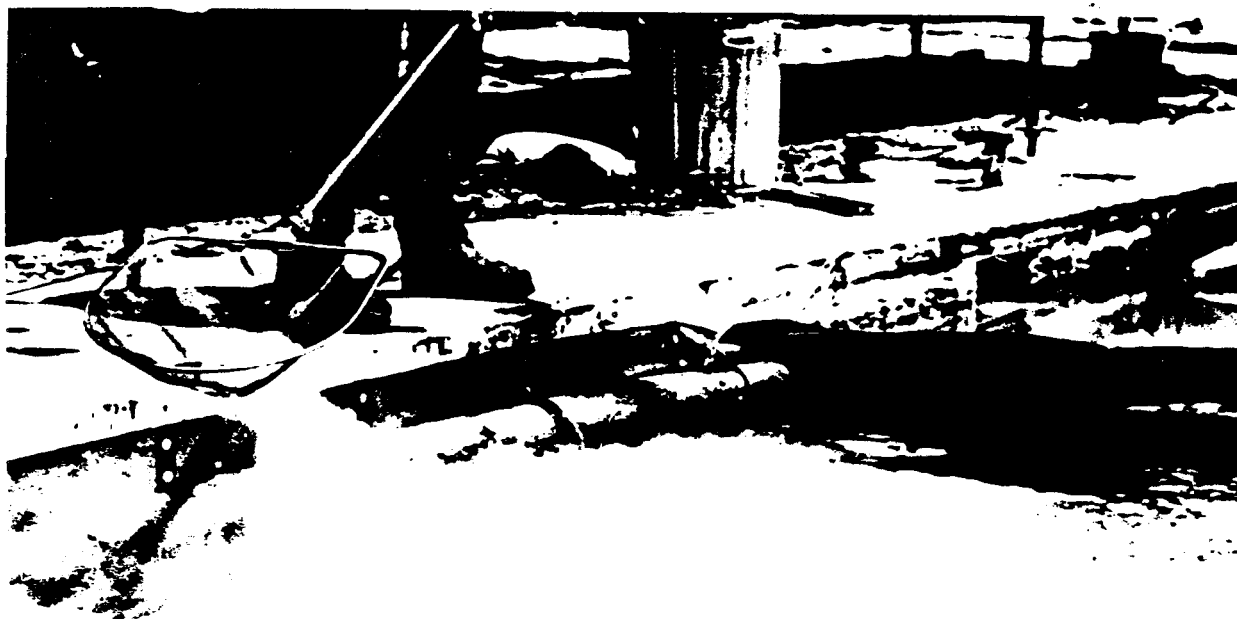


Figure 3. Gelation occurs quickly.

Rapid gelation is essentially completed before carbonation has been completed.



Figure 4. Harvesting gelled oil.

A good idea of the firmness of the gel can be obtained from this picture. It can also be noted that recovery of the gelled oil is virtually complete, using this technique; there is no residual sheen. The clarity of the swept water area is indicated by the vividness of the details on the bottom of the pool (water depth was 8 feet). The greatly increased visibility of the gelled oil is also apparent here (compare with Figure 2).



Figure 5. Detail of gelled oil.

It can be noted here that the thickness of the oil has more than doubled, due to the uptake of water into the gel.

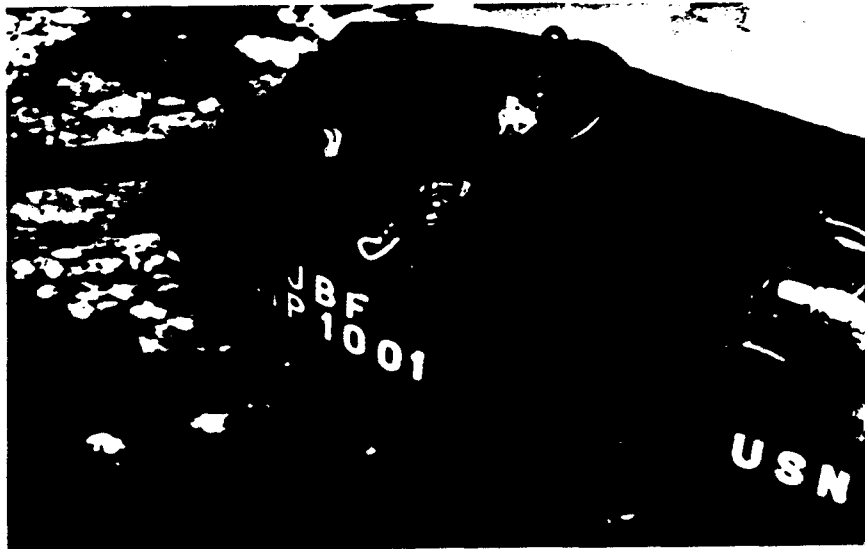


Figure 6. Recovery operation using DIP skimmer craft.

In another test at JBF facilities, with oil gelled by amine carbamate, the following characteristics of the gelled oil can be observed: (1) the gelled oil is relatively immobile; there is little if any tendency for the gelled oil to move away from the recovery craft or to drift back over previously cleared areas. (2) the gelled oil is of much greater visibility than the un-gelled oil, which would considerably facilitate operations, particularly in conditions of low visibility.

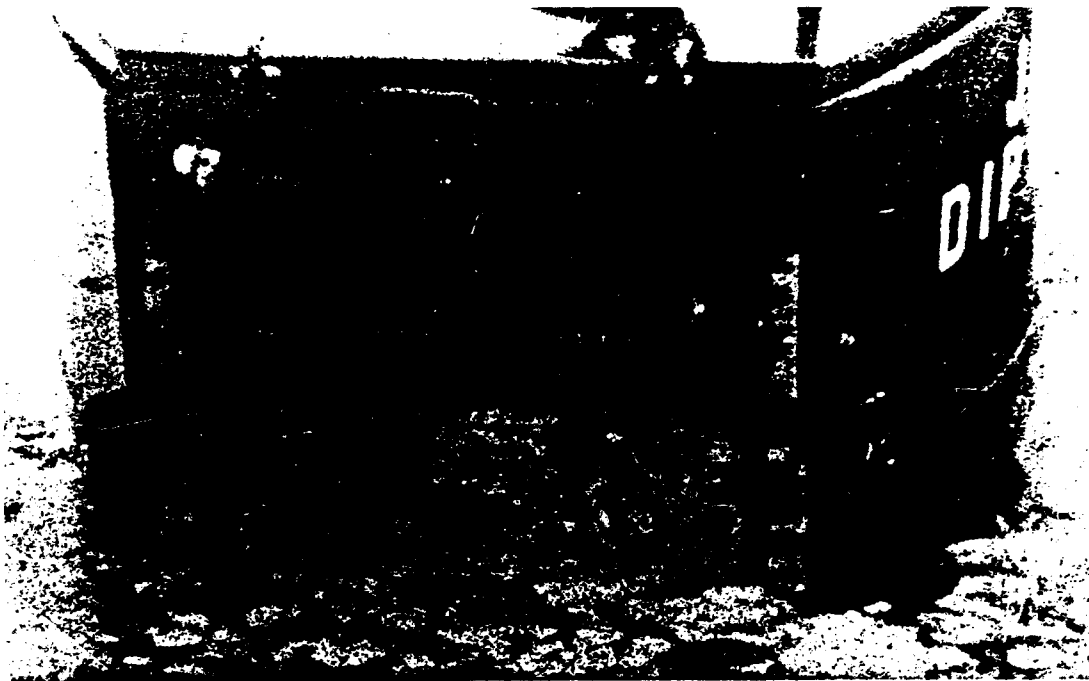


Figure 7. Another view of DIP skimmer.

DIP skimmer in operation on a gelled oil spill. More than 99% of the spilled oil was recovered.



Figure 8. Herding of gelled oil using Navy piston film.

At the end of this first test in the JBF pool facilities, it was found that very small amounts of oil, mostly gelled but with some ungelled oil, had been left behind under boom floats; ungelled oil had apparently escaped the action of the sprayer. This residual oil was treated with Navy piston film (similar in action to Shell "Oil Herder") and then herded by hose action to one end of the boomed area. Total residual oil amounted to less than 400 ml in volume, indicating that a 99% recovery had been effected.

skimmer craft were noted in these tests.

Reference is also made to the following Appendices to this report:

Appendix A: Amine D (Hercules technical report)

Appendix B: Toxicity of Amine D to Marine Life

Appendix C: Toxicology Data Sheet (2), NOPOL

Appendix D: Volatility and Flash Point Studies

OHMSETT TEST I: EXTRAPOLATION OF AMINE CARBAMATE SYSTEM TO LARGE-SCALE SITUATIONS

For the OHMSETT feasibility tests it was determined that a 12- by 100-foot lane at the OHMSETT tank would be boomed off for all test runs (in actuality, a 14- by 117-foot lane was provided during the tests). Accordingly, two 6-foot sprayers, a dry ice crusher-spreader, and a surface breaker for mixing the oil and amine after spraying were constructed and tested at the University of Lowell for subsequent reassembly at the OHMSETT site. All University of Lowell tests were performed in a mockup pool 6 feet wide by 20 feet in length, with a 1-foot depth, which was constructed for these tests. Detailed descriptions of these items of equipment, and discussions of the assembly and operation, are provided with photographic illustrations in Figures 9 through 14 of this report.

A series of 10 tests, under calm, 2-foot harbor chop, and 4-foot harbor chop conditions were originally planned, with both light and heavy CIRCO oils (which were used as simulants for light and heavy commercial oils); in the wave tests, two runs were originally scheduled for prolonged wave action of several hours.

As it transpired, the CIRCO simulants were not optimum choices for the tests. CIRCO oils (as manufactured by the Sun Oil Company) are alicyclic (naphthenic) hydrocarbon-based lubricants, which are significantly different from conventional commercial oils that are mainly noncyclic aliphatic with some aromatic components. Both noncyclic and aromatic hydrocarbons have been found to be readily gelled by amine carbamate gelling agents; low-molecular-weight naphthenic hydrocarbons also are readily gelled, but it appears that this is not the case for the higher naphthenic homologs. Thus, the heavy CIRCO oil was found to be hardly susceptible to gelation, and therefore all OHMSETT tests with such oil were cancelled. The light CIRCO oil did gel, using laboratory samples, although the resulting gel was somewhat weaker in gel strength than is the case with No. 2 fuel oil or similar commercial oils. The CIRCO oils were dyed red for greater visibility during the test; the red dye somewhat obscured the very greatly lightened appearance which normally accompanies the gelation of undyed compositions.

Weather conditions included rain, high humidity, and strong breezes (13 knots the first day, and up to 20 knots the second). Thus, conditions often to be expected in open water situations were well represented in the tests.



Figure 9. Pump for delivery of Amine D solution to sprayers.

Berghofer 2-hp, 1740-rpm direct-drive gear-tooth pump used to deliver Amine D solution to sprayers. Intake is shown from 5-gallon container of amine solution. Rate of delivery for typical Amine D solution: 7 gallons/minute. Power is supplied from OHMSETT bridge at 110 volts.

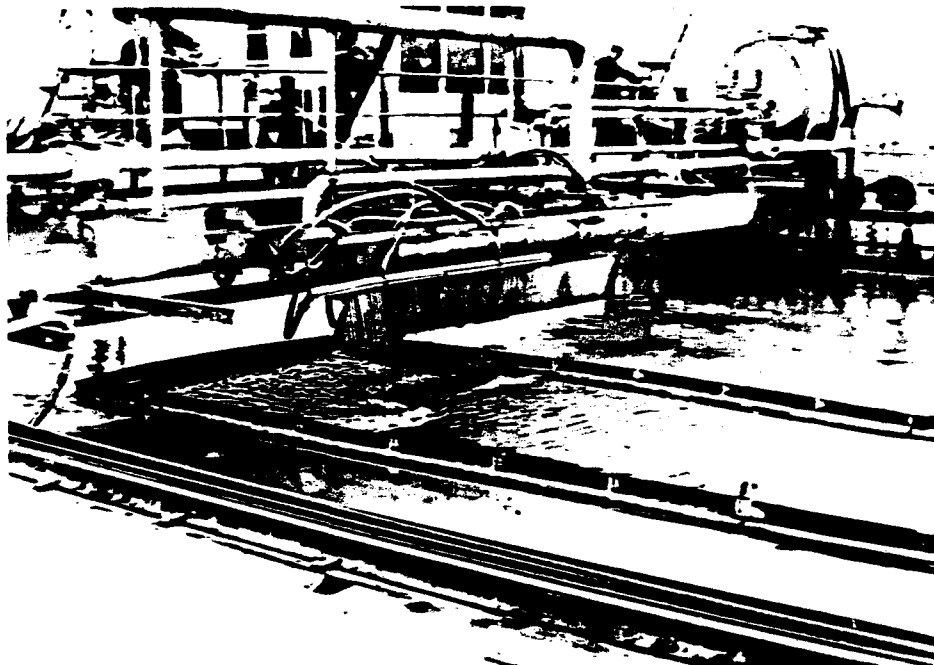


Figure 10. OHMSETT sprayers in action.

Sprayers are two 6-foot sections of 7/8-inch Schedule 40 PVC tubing with 1/32-inch holes at intervals of 1/2 inch. Sprayers are on a "T" mount, and are connected to the Berghofer pump by Tygon tubing.

In this test, under calm water conditions, a boomed-off area of 12 feet by 117 feet was layered with 79 gallons of CIRCO light oil dyed red for greater visibility, with a mean depth of 2.3 mm. Thirteen-knot winds tended to blow oil into patches. In the view above, 14 gallons of Amine D solution (70% amine) is being sprayed over the area, for an average concentration of about 15%. Good lateral coverage was obtained, boom to boom. Longitudinal coverage was hampered by too fast an initial spray rate, with heavy initial doses and light final doses, and also due to patchiness of the slick due to wind action. Despite these problems, very good gel formation occurred, as can be seen in Figure 13.

After each operation the sprayer was cleaned with isopropyl alcohol. Despite this cleaning, spray holes tended to become plugged due to amine carbamate forming on exposure of the contaminated tubing to atmospheric CO₂ over long periods of time. Based on this observation, in future tests disposable sprayer assemblies constructed of the cheap PVC tubing with machine drilled spray holes were used.

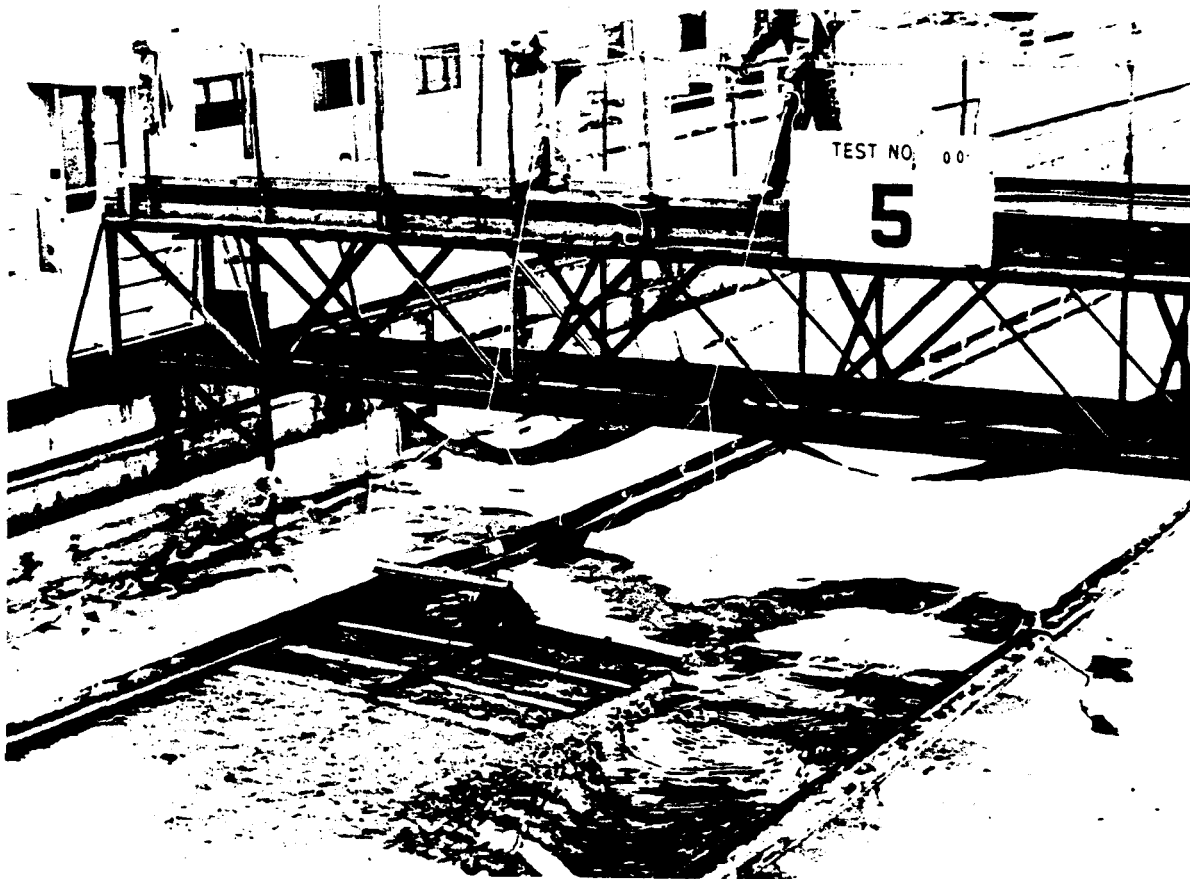


Figure 11. Surface breaker equipment.

Mixing of oil and amine solution using surface breaker as suggested by Dr. William Garrett of NRL and constructed at the University of Lowell using 3/8-inch Neotex matting stretched onto wooden 2-inch by 4-inch boards, each 4 feet in length. The surface breaker was obviously too narrow; an attempt was made to provide complete mixing as much as possible by repeating the passage of the rig over the other side of the area which had not been effected in the first pass.



Figure 12. Application of powdered dry ice.

A plywood hopper was mounted on the moving bridge over the OHMSETT tank. At the bottom of the hopper a motor-driven longitudinal grinder/spreader was installed which further pulverized the crushed dry ice and caused it to be distributed over the spill area previously treated with Amine D solution (see Figures 10 and 11). Rate of distribution was controlled by the variable-speed motor.

Moisture from rain, spray, and high humidities caused frequent disruptions due to clumping of the dry ice granules. A large proportion of the crushed dry ice was not retained on the water/oil surface, but fell through into the water column.

In each run, from two to three 55-pound bags of dry ice were crushed and distributed through the hopper.

Despite the unevenness of the distribution, excellent results were obtained, at least in the calm water tests (in harbor chop tests, poor boom control resulted in excessively uneven boom widths and concomitant very poor control in administration of sufficiently even dose rates of amine solution).

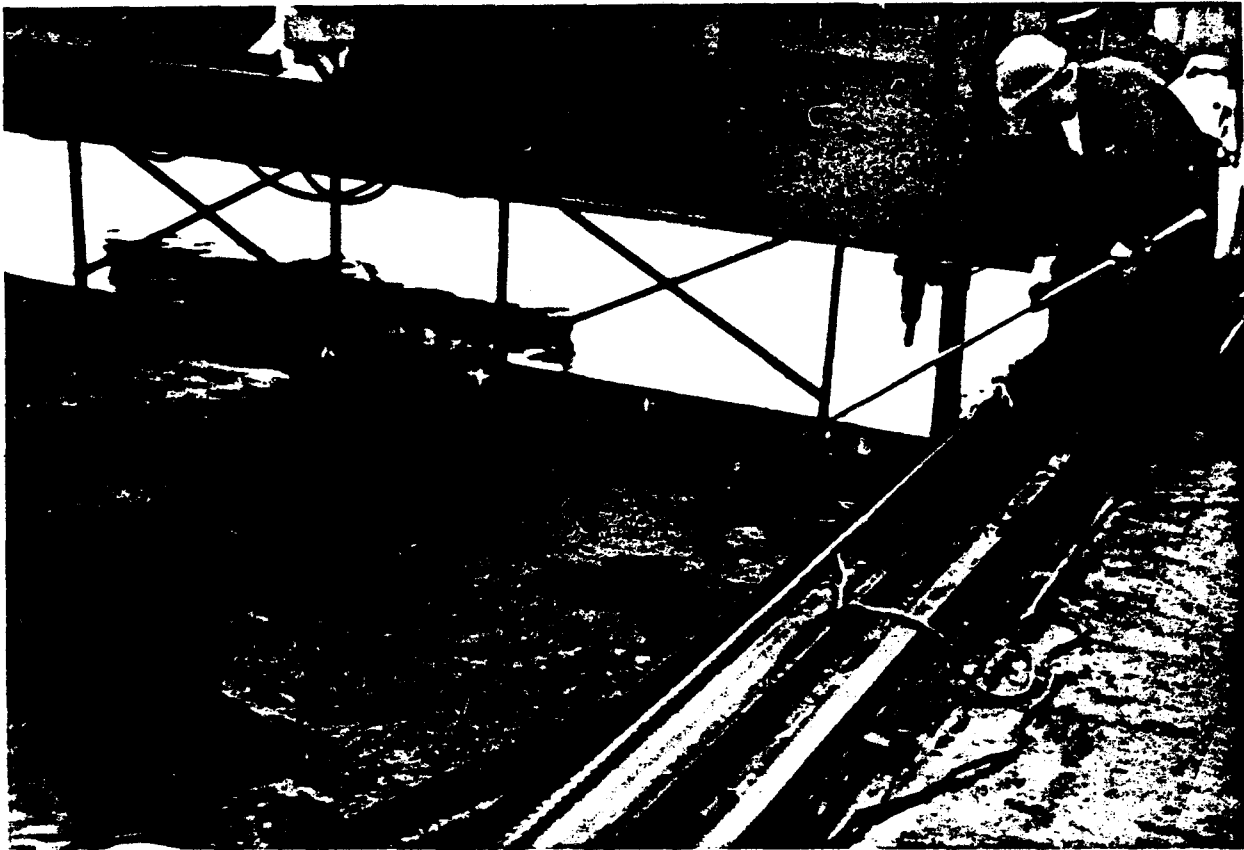


Figure 13. Recovery of gelled oil by means of nets.

Conventional, ungelled oil would be impossible to recover using nets or sieves. (Recovery was also shown to be feasible by means of mechanical suction devices floating in the middle of the gelled oil.)

Essentially complete recovery of the oil was observed, with no residual residues of the red dyed oil noticeable after the completion of the test.

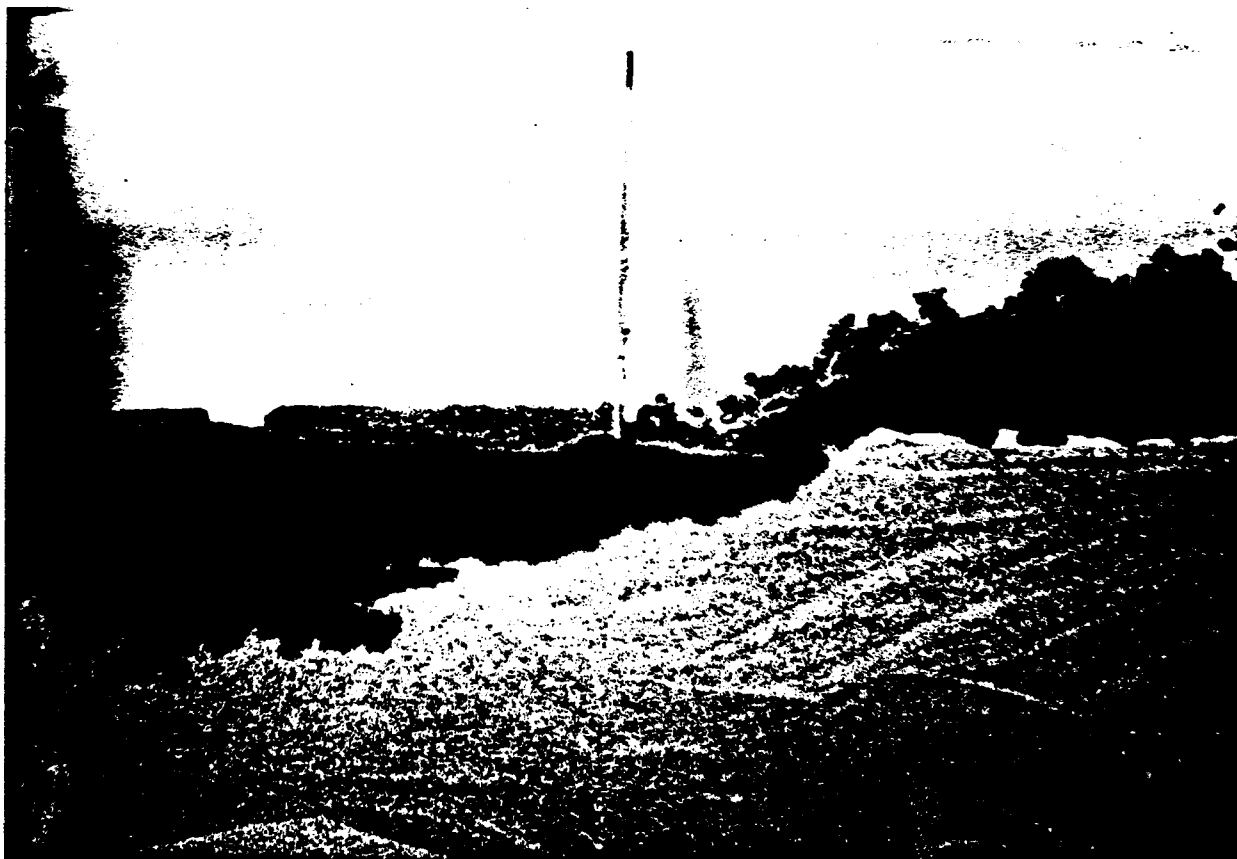


Figure 14. Sand permeability of gelled versus ungelled oil.

A 30- by 12- by 12-inch aquarium was half filled with dry white beach sand, with a glass plate dividing the two halves of the tank, resting in the midsection on the surface of the sand.

100 ml of dyed No. 2 fuel oil was poured in the left portion of the tank; 100 ml of gelled No. 2 fuel oil was placed in the right portion.

The gelled oil remained completely on the surface of the sand, with no permeation. The ungelled oil permeated the sand (with, as can be seen, some lateral permeation into the area underlying the gelled oil). (Time: 5 minutes after pouring, for both samples.)

The following conclusions were derived from these OHMSETT tests:

1. Although the gelled CIRCO oil was of lower mechanical strength than that of conventional gelled oils, it did not spread on the water, but remained controlled in rather rigid patches.
2. The gelled oil was easily recovered, using nets--a capability that would have been impossible for ungelled oils.
3. The gelled oil was not absorbed onto and into the concrete decks of the OHMSETT facility. In further tests performed after return to the University of Lowell, the lack of absorption of gelled oil into sand was noted (see Figure 14). This could be an important consideration in terms of beachfront protection.
4. Using pressure filtration (1 atm as available in vacuum filtration), more than 80% recovery of the oil from the gel was achieved. In subsequent higher pressure (approximately 200 psi) filtration systems, more than 90% recoveries were realized. The oil was free of detectable concentrations of Amine D and of Nopol; these gel components were held in the filter cake. The Amine D carbamate was readily reconverted to the free Amine by boiling in water, thus liberating the CO₂ from the carbamate adduct. The recovered Amine D was determined to be completely effective in subsequent gelation tests.
5. It was obvious that water in the form of rain, spray and high humidity was quite deleterious to the usage of crushed dry ice as a carbamating agent. This, coupled with the obvious problems involved in procurement and storage, made future use of dry ice a highly infeasible feature in the gelation process for use in control and recovery of oil slicks. Future work was thus predicated on the feasibility of using carbon dioxide in liquid/gas form as is available in commercial CO₂ cylinders and tanks.

BAY "F" TEST I: CARBAMATION BY LIQUID/GASEOUS CO₂ SYSTEMS

Based on the new requirement for a carbonating system that would not depend on solid dry ice, work was therefore initiated in January 1978 on use of pressurized CO₂ cylinders or tanks for this purpose. A test pool was constructed at the University of Lowell for preliminary studies toward this end, and gaseous CO₂ carbonators were constructed for use with the OHMSETT sprayers.

As a result of these tests, a final field test was performed at the Bay "F" tank at the EPA's Edison laboratories. Although considerably smaller than OHMSETT (the Bay "F" tank was 100 feet long, about 12 feet in width, and 4 feet deep), it presented excellent cold-weather test capabilities. Equipment designed and constructed at the University of Lowell was utilized in the Bay "F" tests. Excellent results were obtained, and these are presented in Figures 15 through 17. Conclusions drawn from the Bay "F" Test I exercises are as follows:

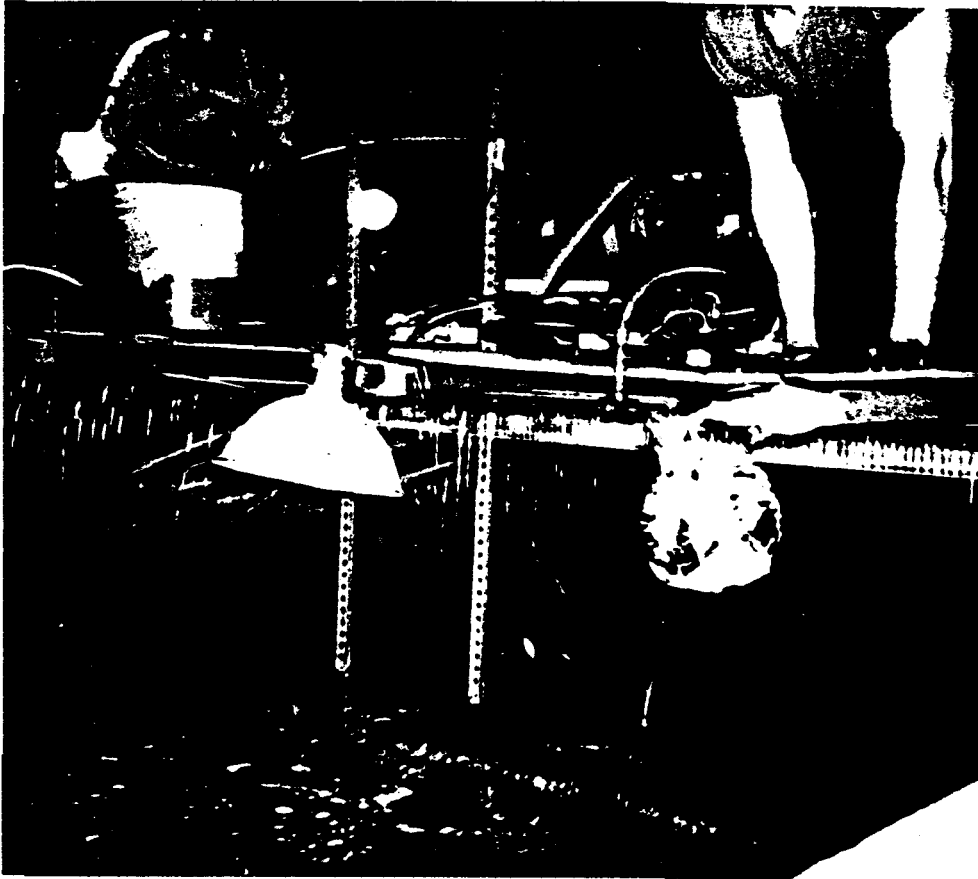


Figure 15. Spraying operation at Bay "F" Test I.

The 12- by 100-foot Bay "F" tank was layered to a depth of 2 mm with 55 gallons of No. 2 fuel oil. Two OHMSETT-type sprayers (see Figure 10) were mounted on the tank's moving bridge, as were two CO₂ underwater bubblers constructed from 6-foot lengths of 4-inch Schedule 40 PVC pipe drilled with 1/32-inch holes 1/4 inch apart in five lines 1 inch apart. The pipes were plugged at each end with a 7/8-inch PVC inlet at the centers. Each carbonator was connected to a Size 1A CO₂ tank holding 60 pounds of CO₂ at 830 psi. The regulator of each tank was electrically heated to prevent freeze-up. CO₂ tanks, Berghofer pump (see Figure 9), and Amine D drums were carried on the deck of the bridge. 10.5 pounds of Amine D solution was sprayed on the oil to provide a 16% solution (11% in terms of the 70% Amine D concentration in the solution).



Figure 16. Carbonation at Bay "F" Test I.

After spraying with the Amine D solution, CO₂ was bubbled from the carbonating pipes; gelation occurred almost at once. A total of 80 pounds of CO₂ tanks. The theoretical weight needed for 10.5 gallons of Amine D solution (70% Amine D) is 9.4 pounds of CO₂. Again, most of the CO₂ gas lost to the atmosphere.

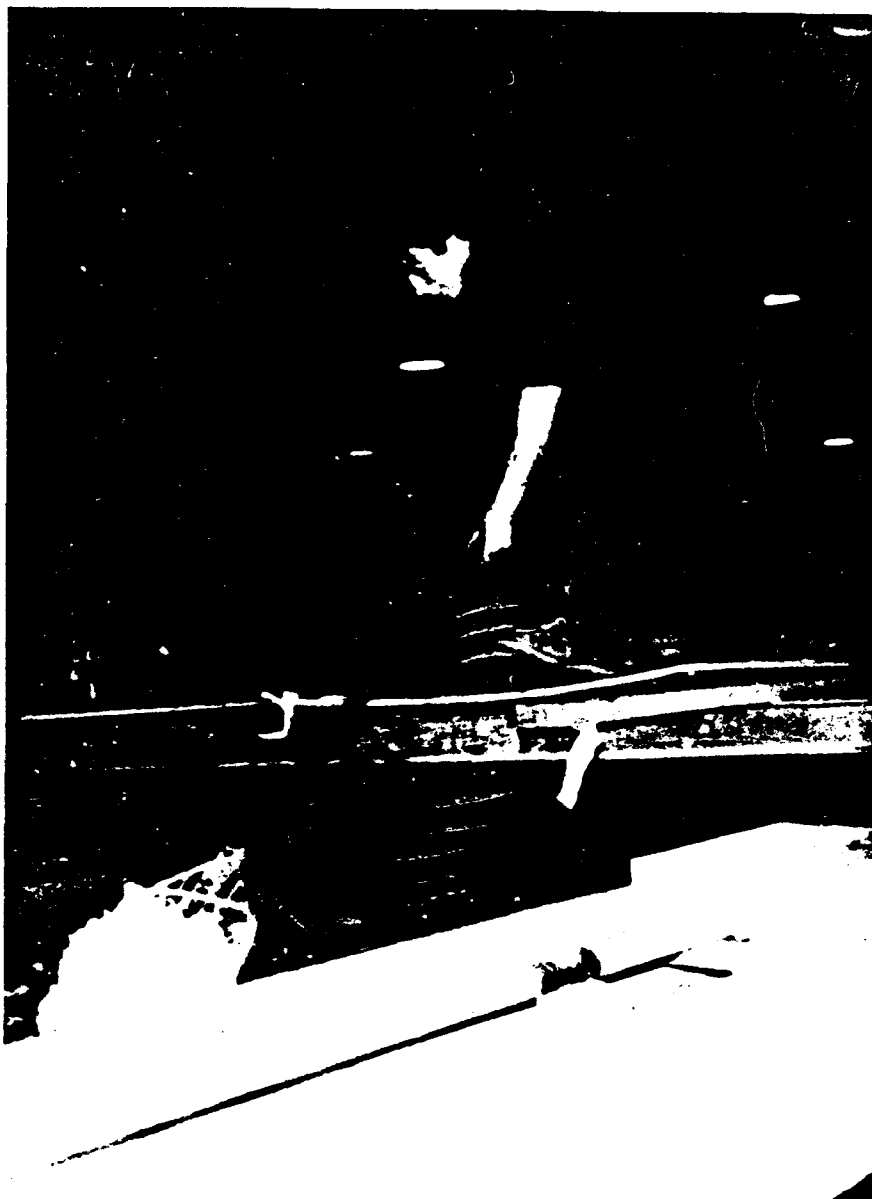


Figure 17. Recovery of gelled oil by means of sieve.

The gelled oil was recovered manually by means of a sieve and was collected in a barrel (not shown in this view). The recovery was complete, with no sheen on the water surface. (Some residual oil that was on the water surface from a previous and unrelated test was also removed from the surface, with the result that the water surface was cleaner after this test than it was before adding 55 gallons of No. 2 fuel oil.)

1. Commercially available liquid CO₂ in cylinders or tanks (in this test delivered in gas form) is an excellent carbamating agent with none of the disadvantages observed in the OHMSETT use of dry ice.
2. Improved Amine D sprayer systems were designed and tested.
3. It was apparent that a two-pass system (with separate phases involving application of Amine D solutions as a spray, followed by a subsequent pass with application of CO₂) would be infeasible in field operations. Future tests would thus be predicated on a single-pass requirement in which spraying and carbonation would be conducted simultaneously.
4. About 10 times the theoretical requirement for CO₂ was utilized in the Bay "F" Test I, with much of the CO₂ being lost to the atmosphere. Although CO₂ is a rather cheap commodity, for large-scale operations it would be highly desirable to have equipment that would permit maximum contact of the CO₂ with the Amine D gelling agent in the oil, to minimize reagent payload requirements on the control craft.

OHMSETT TEST II: DESIGN, CONSTRUCTION AND TESTING OF PROTOTYPE SPILL CONTROL AND RECOVERY EQUIPMENT

Based on the requirements for a one-pass (simultaneous amine spraying and carbonation) capability, and for equipment that would optimize the contact time for interaction of the CO₂ and Amine D, work was initiated in the Spring of 1978 in the design and testing of such systems. We also wished to provide a capability for large area (approximately 1 acre) coverage in a single pass over a short interval of time (about 15 minutes or less), with a craft that could be used in open-water harbor conditions presenting wave heights up to 2 feet.

Most of the preliminary test work on this phase was performed at the Massachusetts Maritime Academy at Buzzards Bay, Massachusetts, using their auxiliary small craft, boat shop and other facilities. A 26-foot motor whale boat ("Compass Rose") was provided for this preliminary work, and also for final testing at the OHMSETT facility.

Spraying equipment was substantially the same as for the previously described exercises, except that the 70% Amine D solution was held in 17-gallon beer kegs (eight of these stowed in the forward portion of the boat) with air pressure from a SCUBA tank utilized to force the amine solution through the sprayers. Sprayers were mounted outboard from the bow of the boat.

Canvass tarpaulins were stretched over port and starboard frames to provide carbonator chutes, the role of which was to maximize contact time for the interaction of amine and CO₂, thereby minimizing the amount of CO₂ required for complete carbonation. CO₂ was provided from a 1000-pound (empty weight) transit tank, laden with 750 pounds of liquid CO₂, which was delivered in liquid form by pressure hoses leading to the forward ends of the carbonator chutes, under water.

An improved portable, hand-operated pressure filter apparatus was con-

structed and shown to be effective in extracting more than 90% of the original oil, uncontaminated with amine or nopol constituents, from the gelled oil recovered in the OHMSETT exercises.

The results of this test are shown in Figures 18 through 26. The summary conclusions derived from this test series are as follows:

1. Large spill areas (an acre or more) could be treated and controlled quickly (within 10 minutes) by use of this craft, which can contain up to 400 gallons of amine solution and 750 pounds of CO₂. Complete recovery of the resulting gelled oil could be effected in about the same time interval by means of followup craft equipped with suitable netting gear.
2. Excellent results were obtained in smooth water conditions. Gel time was 2 minutes or less, and there was a high rigidity associated with the gel. Recovery by nets was exceptionally easy.
3. For other than smooth water conditions, e.g., in harbor chop conditions, further attention needs to be given to design of the sprayer/carbonator assemblies. Specifically, the interaction of confused seas with the bow wave of conventional harbor craft tends to force a large amount of incoming oil in the intended track of the craft to either side and away from the reach of the sprayer/carbonator assemblies. To avoid this, one solution would be to mount these assemblies further forward and further outboard of the craft. Another suggestion would be to mount intake booms, as are situated on most skimmer craft, to direct incoming oil more directly into the paths of the sprayer and carbonators.
4. Although such a craft would be useful in harbor or in similar situations where storage and maintenance of the craft would present little problem, a need could exist for a portable spill control and recovery craft that could be easily assembled and disassembled, and that could be easily stored and transported in a trailer to remote spill areas from a central location.

BAY "F" TEST II: DESIGN, CONSTRUCTION, AND TESTING OF PROTOTYPE PORTABLE SPILL CONTROL AND RECOVERY EQUIPMENT

In this test a small, three-man rubber raft was modified to provide a small-area spill control and recovery craft that could easily be stored and transported to remote spill sites. In the small confines of the Bay "F" test pool, very good results were obtained, suggesting that the craft would be of use in possible remote spill situations, particularly in inland waters with little or no wave action.

The raft was equipped with right- and left-side fold-up sprayers (which could be raised and lowered to accommodate maneuvering requirements in obstructed areas) and which were fed from canisters of the type used for dispensing soft drink concentrates in soda fountains. The Amine D solution was directed into the sprayers from the canisters under pressure from a SCUBA

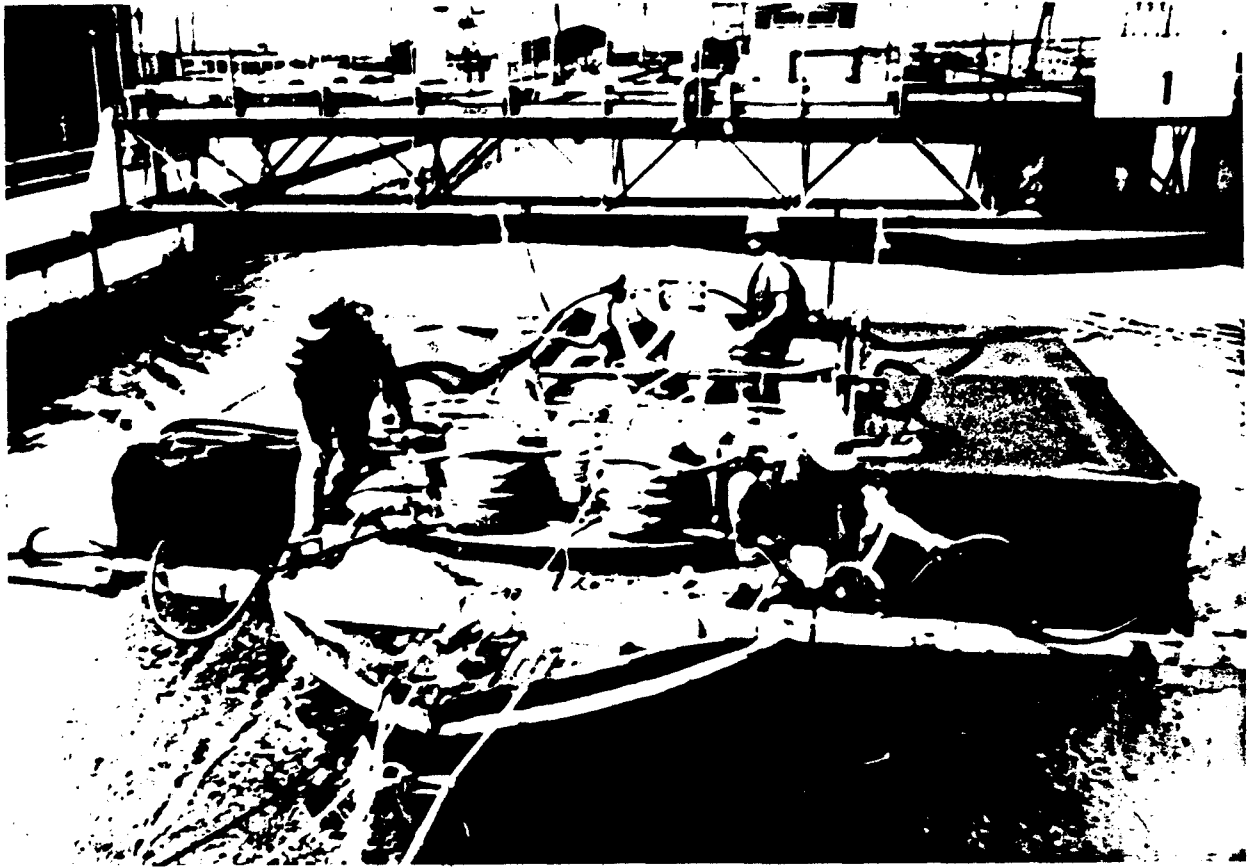


Figure 18. "Compass Rose" underway in OHMSETT tank.

Diesel fuel is laid down in front of boat; amine solution is sprayed directly in front of canvas chutes; CO_2 (in liquid form) is introduced under the water in each chute to convert the oil/amine mixture into gelled oil. Beer kegs in foredeck of boat contain amine, under pressure; 1700-pound transit tank in rear of boat delivers CO_2 .

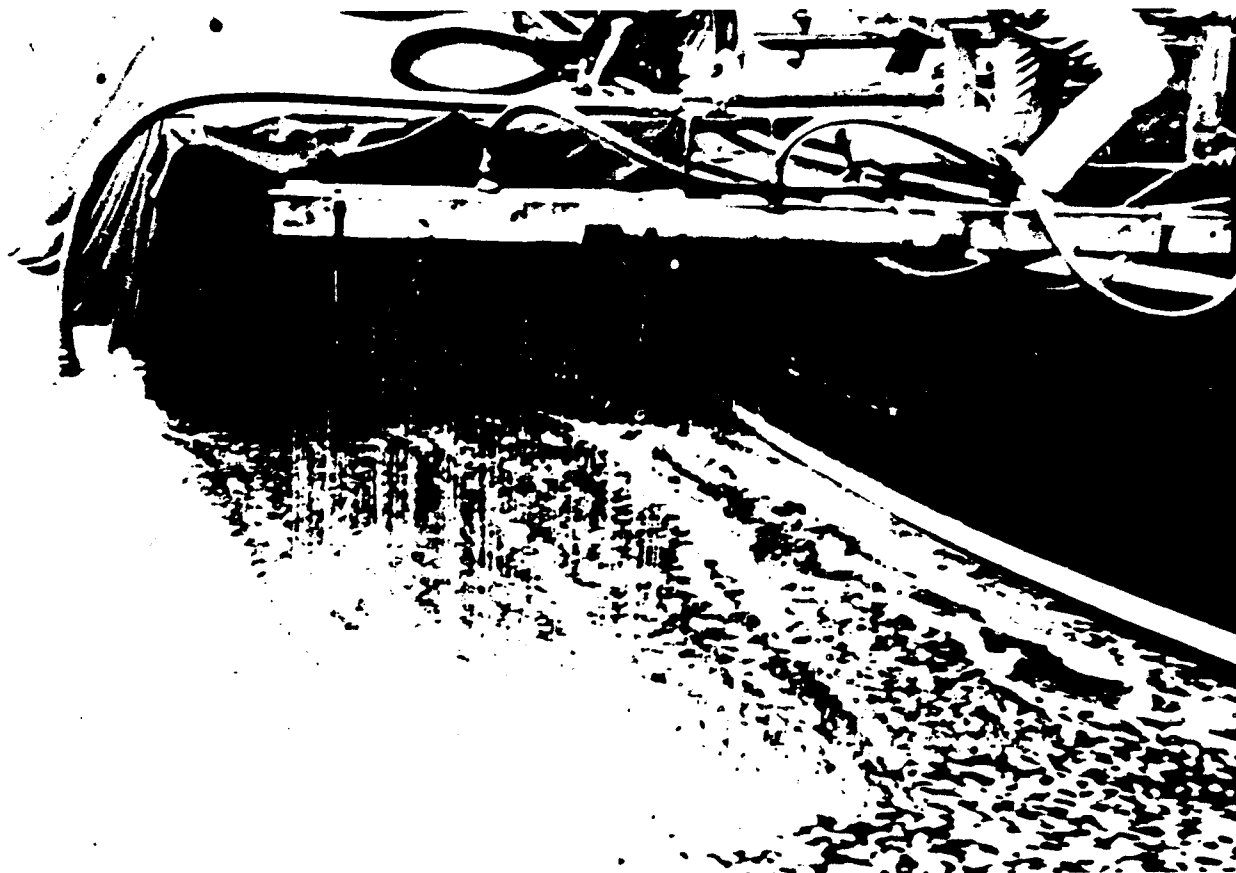


Figure 19. Spraying apparatus on "Compass Rose".

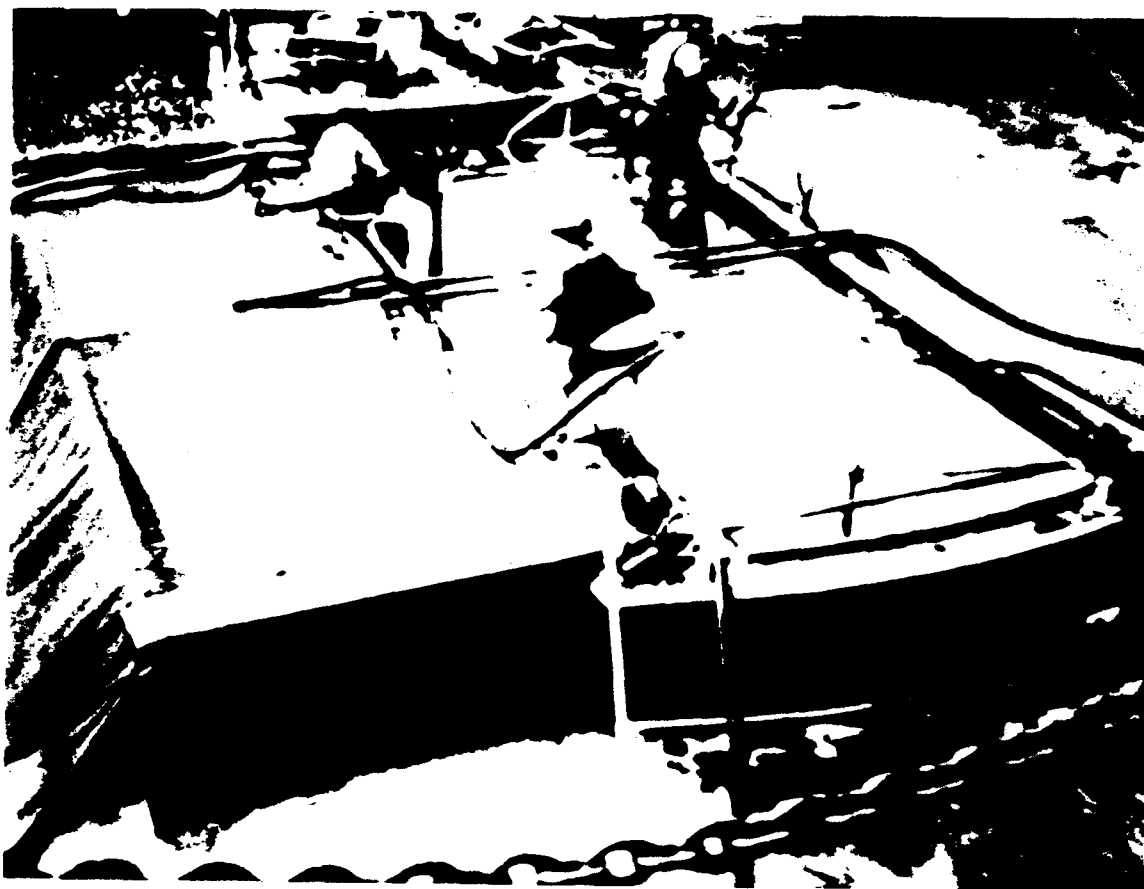


Figure 20. Carbonation from "Compass Rose".

"Compass Rose" underway in OHMSETT tank at 2 knots. Diesel fuel (dyed red for greater visibility) is being laid down in front of the boat; Amine D solution is being sprayed over the slick as it enters the carbonator chutes on each side of the boat; CO_2 (in liquid form) is sprayed from under the water in each carbonator chute to convert the oil/amine mixture into gelled carbamate.

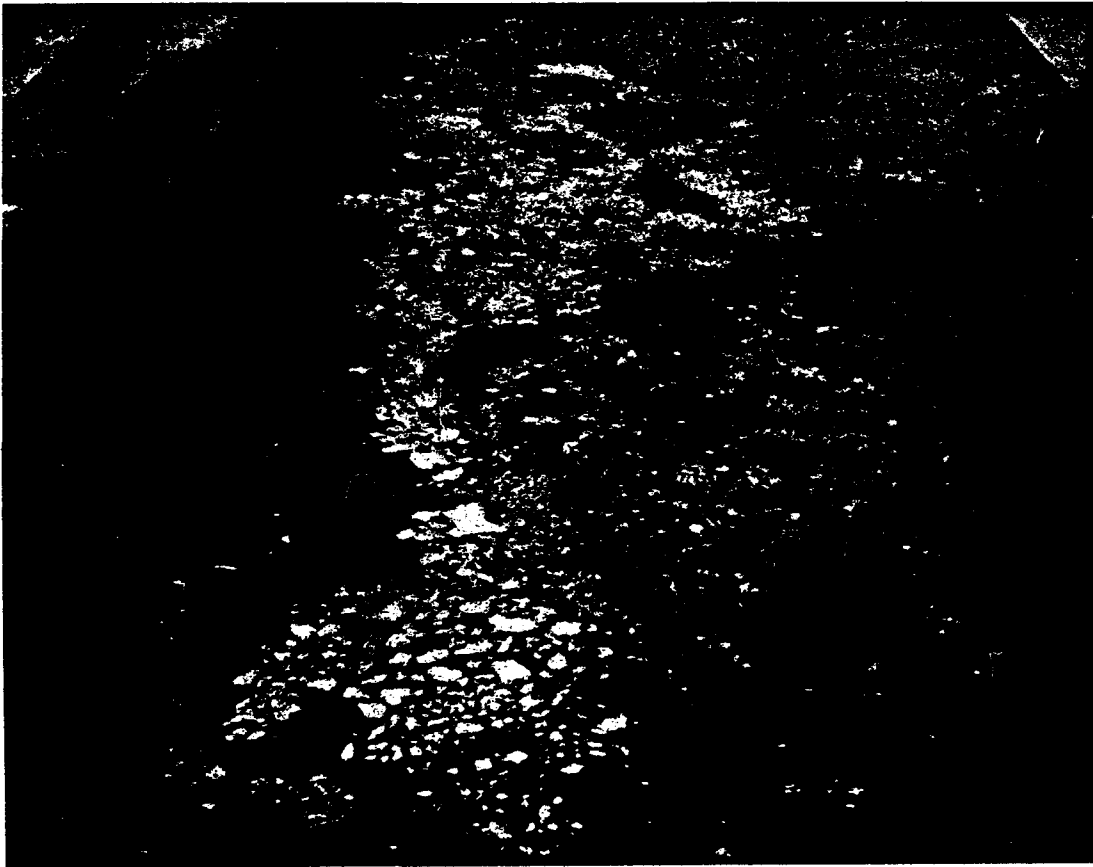


Figure 21. Gelled oil in OHMSETT tank.

The gelled oil as it appeared in the wake of the "Compass Rose." Gel time was about 2 minutes.



Figure 22. Gelled oil in OHMSETT tank.

The gelled oil as it appeared being pushed down the length of the OHMSETT tank. The gelled oil was in the form of rigid plates.



Figure 23. Recovery of gelled oil by net.



Figure 24. Portable hand-operated filter press.

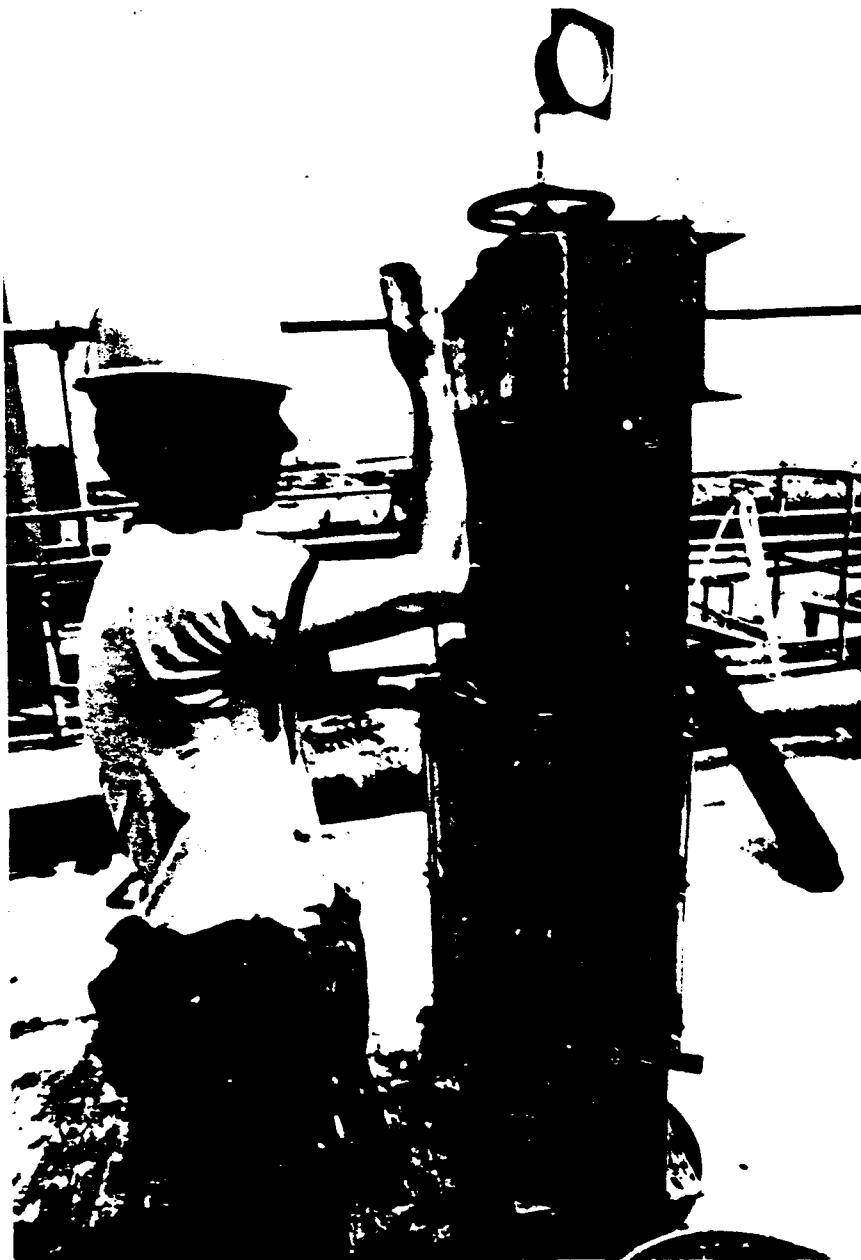


Figure 25. Filter press in operation.

More than 90% of the original oil was extracted from samples of gelled oil used in this apparatus. The extracted oil was free from contamination by Amine D and Nopol gelling agents.

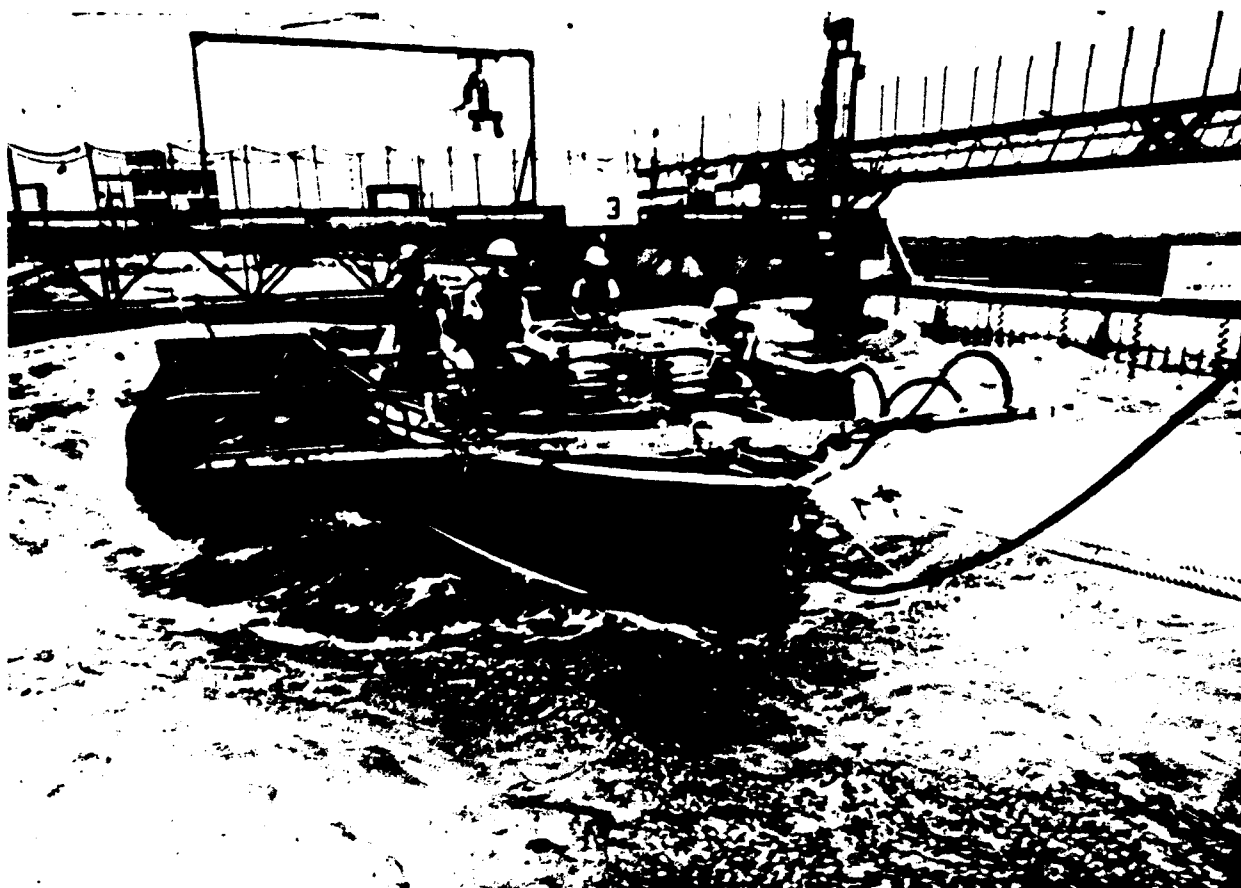


Figure 26. Wave action effects on "Compass Rose" intakes.

Test under way at 2.5 knots with a 1-foot harbor chop. Wave action caused part of the oil to be swept beyond the chutes on each side of the boat; therefore, only that portion of the oil entering the chutes was subjected to carbonation, and the remaining oil was ungelled. Bringing the chutes forward to a position just abaft the sprayers should substantially rectify this problem.

tank carried on the raft. The canisters were carried in racks slung from the raft on both sides, which racks also held CO₂ bottles of the type used in some fire extinguishing systems and routinely used for dispensing carbonated beverages.

In the Bay "F" test, separate passes were performed (i.e., an initial amine spraying run followed by carbonation in a second pass). For actual spill situations it was intended that spraying and carbonation would be conducted simultaneously, as was demonstrated on a much larger scale in the OHMSETT II test with the "Compass Rose." The results of this test are shown in Figures 27 through 32.

FIELD TESTS AT U.S. NAVAL SUBMARINE BASE, NEW LONDON, CONNECTICUT

Several tests were performed at this activity in late 1980 and early 1981 in attempts to reduce to practice, in actual oil spill situations, the concepts and techniques that had been developed in the previous test programs.

Results of these tests are shown in Figures 33 through 40. The following conclusions were derived:

1. The small rubber raft developed in the Bay "F" exercise was totally unsuitable for open water work, particularly with the dual capability for spraying and carbonating in one pass. The raft was so overladen that it presented danger of swamping even in small waves of less than 2 feet in open water.
2. The raft might be considered safe and feasible for use in "mill pond" conditions as may be encountered in small lakes or other small bodies of water. Even for such conditions, however, it was considered advisable to have a sturdier craft with higher freeboard and greater stability. Further advantage would also accrue from having increased capabilities for larger spills as a result of the larger capacity for gelling agents which such a larger craft could carry.
3. In subsequent tests at the Submarine Base, a trimaran (three-hulled raft) was used with excellent results. This craft was quite stable in wave conditions up to 2 feet. It is quite sturdy, and can easily carry up to 2.5 tons of equipment and supplies, in addition to a crew of five technicians. It is capable of attaining working speeds of up to 5 knots, which would enable coverage of up to an acre of oil spill area to be controlled by gellation in approximately 10 minutes, using gelling equipment and supplies that can be carried on the trimaran. By installation of appropriate intake booms at the bow of the trimaran, bow wave problems (such as were encountered with the Compass Rose involving interaction of the bow wave with confused seas to cause sweeping of incoming oil to be swept to either side of the craft) should largely be eliminated.
4. Further work would be desirable to develop a portable trimaran that could be assembled, disassembled, capable of being stored and transported with all required equipment and supplies in a small van, and



Figure 27. Spraying apparatus in operation at Bay "F" Test II.

The Amine D solution is being sprayed into the oil slick (comprised of about 40 gallons of diesel fuel) with 11 gallons of amine solution being applied. As is typically the case, the oil is barely visible on the water surface, prior to gelation.



Figure 28. Carbonation apparatus at Bay "F" Test II.

After spraying with Amine D solution, the spray cans are removed and replaced with the CO₂ tanks and the amine solution in the oil is subjected to reaction with the CO₂ bubbling up from below the surface of the water.



Figure 29. Gelled oil at Bay "F" Test II.

After 2 minutes the oil is completely gelled and ready for harvesting. Note the greatly enhanced visibility of the gelled oil, and its immobility in the water, both of which factors are of great importance in recovery efforts.

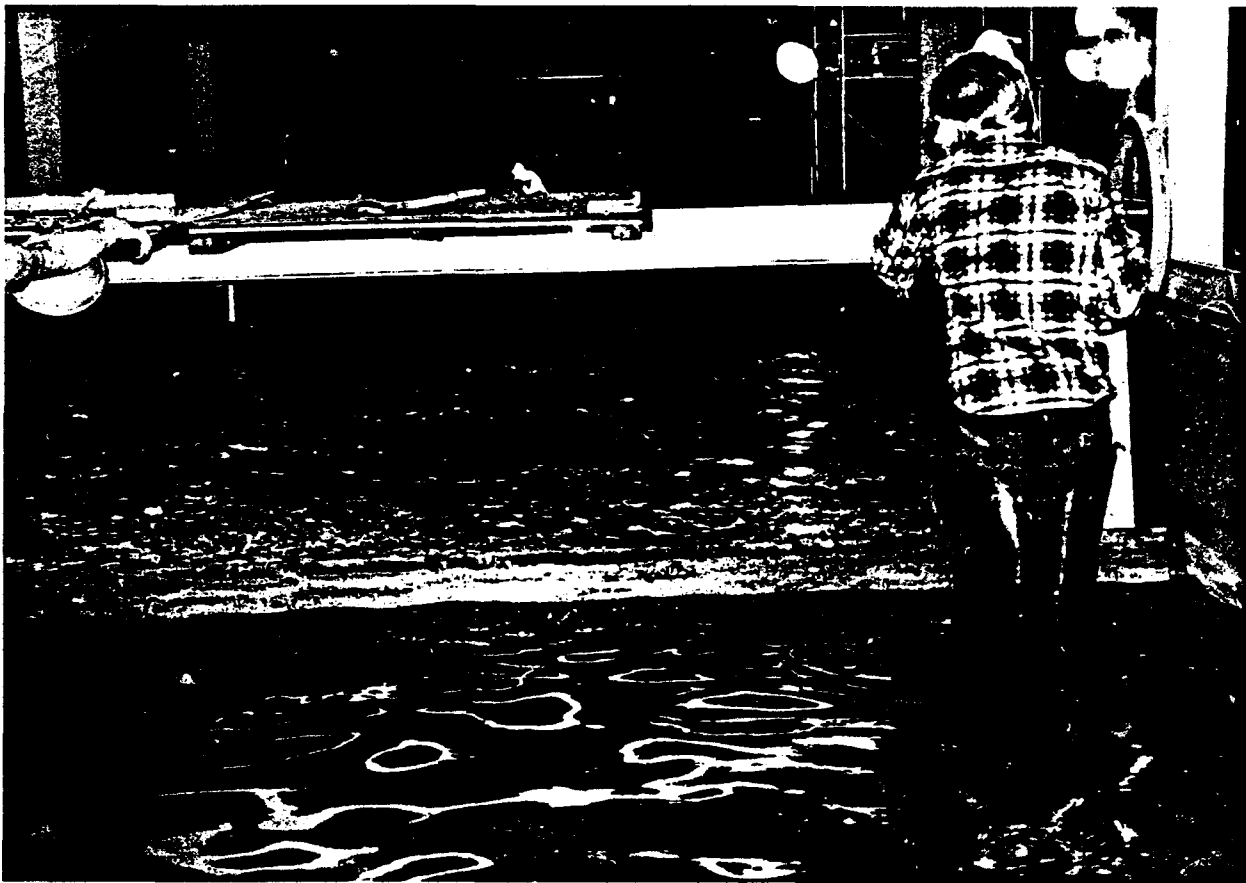


Figure 30. Herding of gelled oil with screen.

The gelled oil is being herded down the tank using a screen fixed to a board. Ordinary nets and sieves are equally effective in collecting the gelled oil.



Figure 31. Gelled oil at Bay "F" Test II.

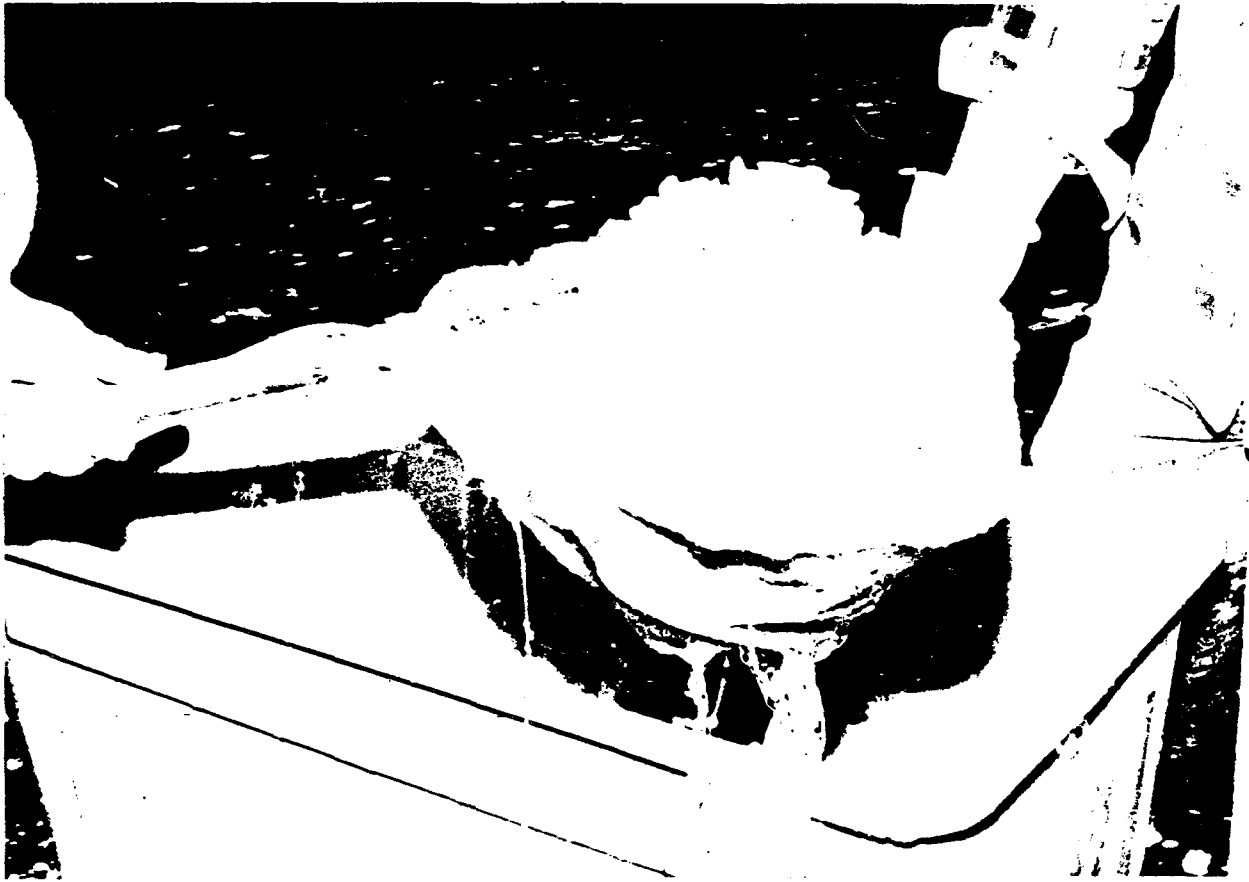


Figure 32. Recovery of gelled oil by net.

Removal of gelled oil using a sieve, an impossible task in the case of ungelled oil. Recovery is virtually complete with this process, versus maximum efficiencies of less than 80% with other processes. Recovery time is much less with gelled versus ungelled oil. The water in this tank was demonstrated to be cleaner after the recovery effort than it was before the oil was originally laid down.



Figure 33. Loading rubber raft assembly at New London Sub Base.

Loading "Titanic" with CO₂ bottles and Amine D canisters. In this view the carbonators and sprayers are folded up.

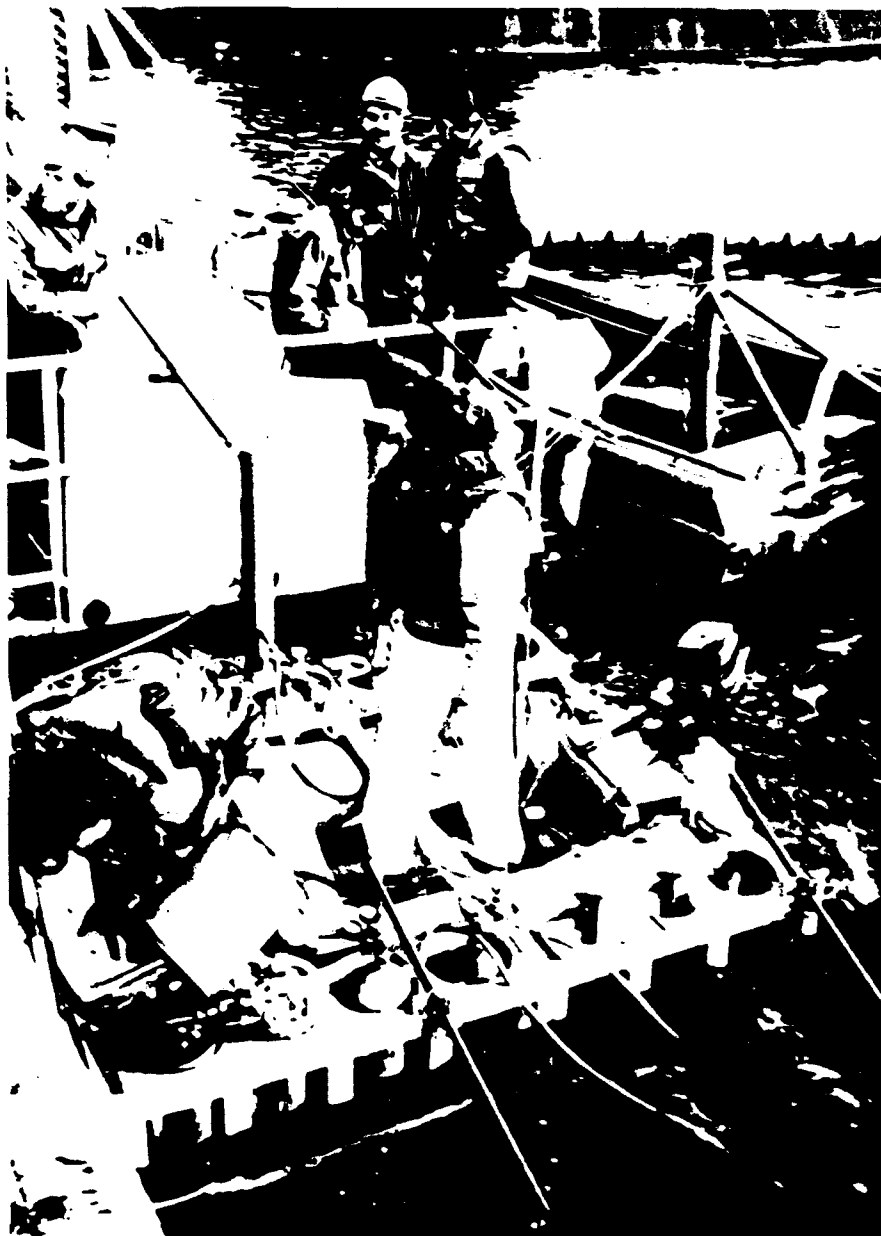


Figure 34. Filling Amine D canisters on raft.
(In this view, the carbonators have been lowered into the water)

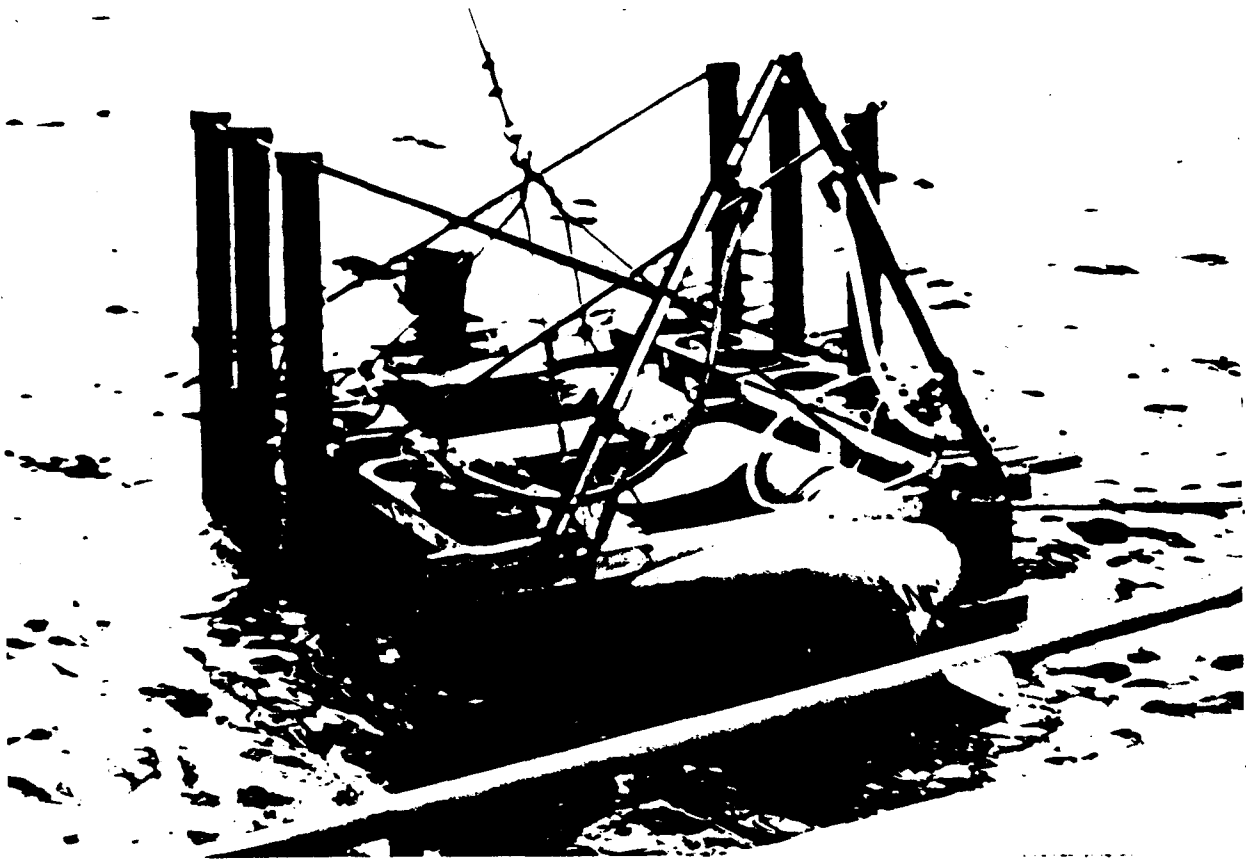


Figure 35. Rubber raft equipped at submarine base.

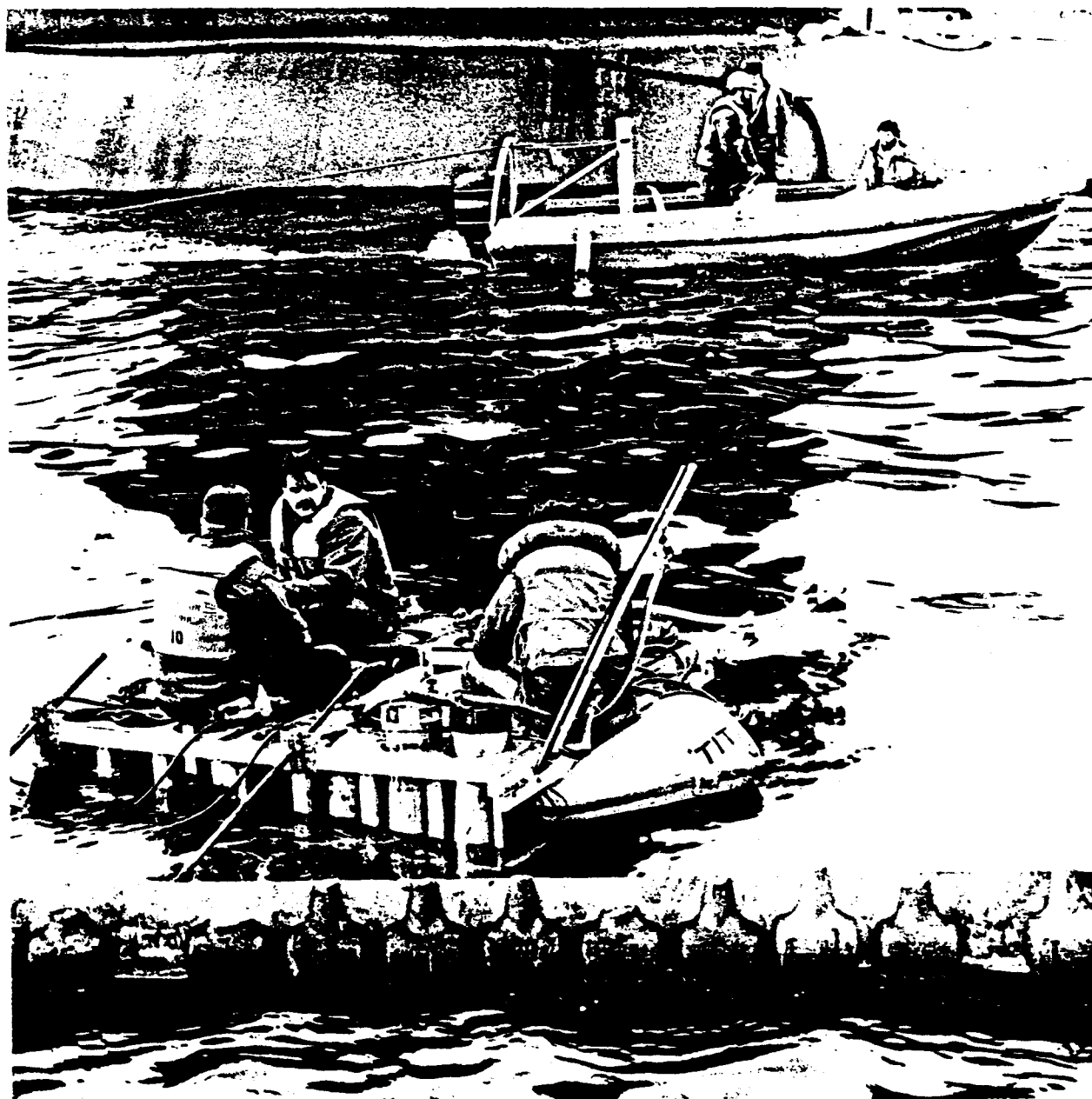


Figure 36. Rubber raft manned, awaiting boom placement.



Figure 37. Raft "Titanic" in operation at submarine base.



Figure 38. Another view of raft operation.

"Titanic" spraying and carbonating. One sprayer has been raised to permit maneuvering in boom area.

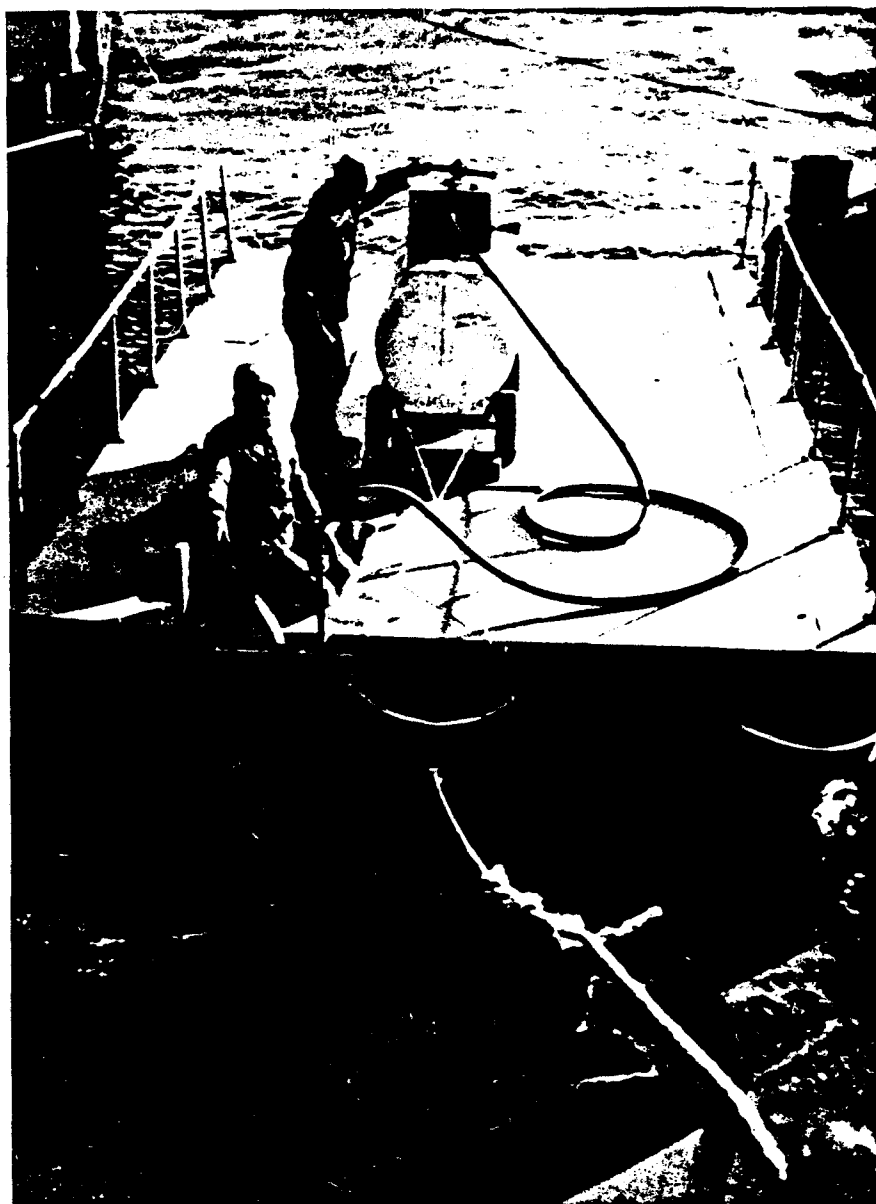


Figure 39. Trimaran craft at submarine base.

Carbonation and amine is being applied at bow. Spaces between hulls, under the deck, provide ample contact time for interaction of amine and CO_2 .

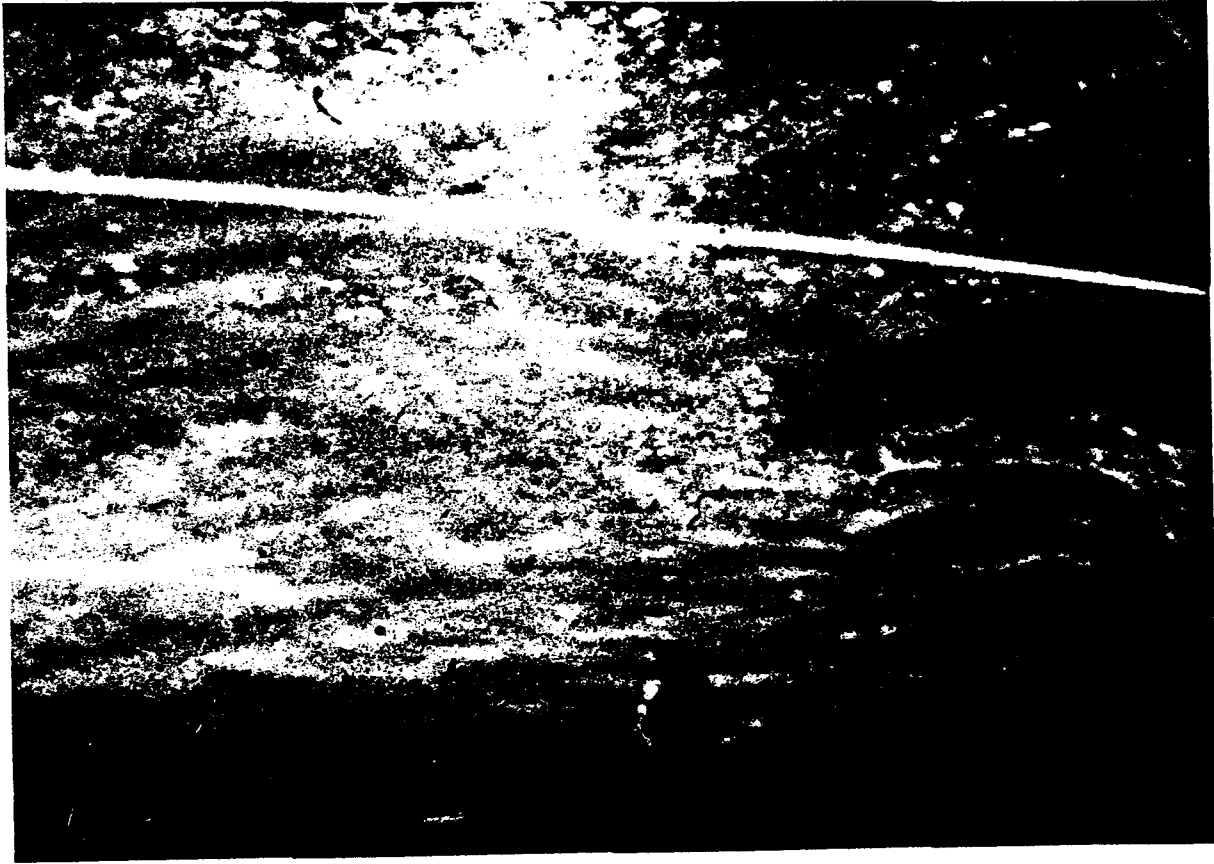


Figure 40. Gelled oil from stern of trimaran raft.

Gelation occurred within 5 seconds of initiation of sprayer and carbonator. Most of gelled oil was collected in 1-inch mesh net (shown at extreme right). Untrapped oil is floating in water behind the net. Combined spraying and carbonating operations is thus feasible and successful in open water situations.

capable of gelling and controlling a large spill area quickly and completely. The use of nets towed behind the craft could enable simultaneous control and recovery of such spills. (See Appendix I for data constituting plans for such a craft. The following additional appendices to this report also contain pertinent information as is indicated):

Appendix E.1: Submission of Product Listing to Canadian Environmental Protection Service regarding Amine Carbamate Gelling Agents

Appendix G: Report of Oil Spill Control and Recovery Field Tests at U.S. Naval Submarine Base, New London, Connecticut.

USE OF FLUORESCENT AGENTS AND ACOUSTIC SENSING FOR NIGHT-TIME SPILL RECOVERY AND CONTROL OPERATIONS

Full-scale research efforts in this direction were instituted in mid-1981, with extension also to sonic sensing techniques in the Fall. In September 1981 a test was performed on the EPA Ocean Survey Vessel ANTELOPE in Cape Cod Bay; a report of this exercise is provided in Appendix H to this report. The following observations and conclusions pertain to this on-going work.

1. Fluorescent agents can be applied in the form of sprays of liquid solutions of such agents, or by dusting with powder formulations. Current tests strongly suggest that the dusting operation is the more feasible, although both techniques have proven extremely promising.
2. Very small (about 50 parts per million) concentrations of fluorescer in oil or hazardous chemical spills are quite effective in providing excellent night-time visibility.
3. The best dust formulations appear to be intimate mixtures of the fluorescer in powdered gypsum (CaSO_4). The optimum spray formulation appears to be a solution of the fluorescer in di- or tri-propylene glycol monomethyl ether solvents.
4. Uvitex OB (TM) (Ciba-Geigy Corp.) and Yellow 131SC (TM) (Morton Chemical Co.) have proven to be excellent nontoxic, cheap, and highly effective fluorescers. (See Appendix C.1 for a description of the low toxicity of Uvitex OB.)
5. Use of the fluorescence system is not confined to petroleum materials. Specifically, all organic chemicals cited in Figure 42 as being most frequently involved in transportation incidents are compatible with the fluorescence system.
6. The gypsum powder base is entirely nontoxic and with no fire or other hazardous effect. Glycol ether solvents have very low fire and toxicity effects, and in the concentrations contemplated for use would probably present no significant hazard. (See Appendices E and J for additional information regarding features and developments

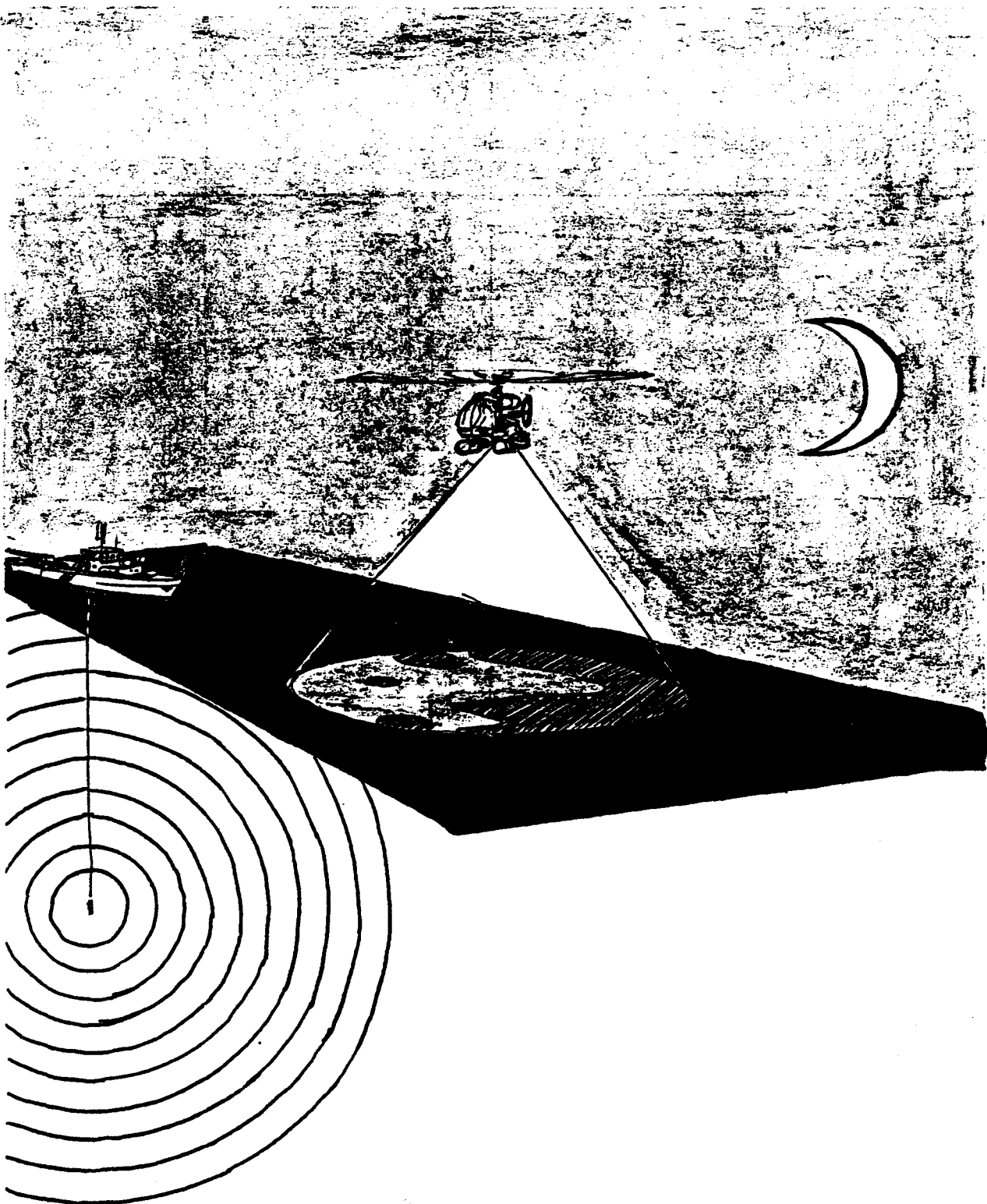


Figure 41. Use of fluorescent agents and acoustic sensing for night-time oil spill recovery and control operations.

Certain chemicals are most frequently involved in transportation incidents

| Commodity | All modes | | | Highway | | | Railway | | |
|-------------------------------------|-----------|----------|-----------|---------|----------|-----------|---------|----------|-----------|
| | Deaths | Injuries | Incidents | Deaths | Injuries | Incidents | Deaths | Injuries | Incidents |
| Paints, enamel, lacquer, and stains | 0 | 28 | 13,304 | 0 | 26 | 13,075 | 0 | 0 | 57 |
| Corrosive liquids | 12 | 306 | 7,959 | 10 | 263 | 7,660 | 2 | 35 | 235 |
| Wet batteries | 0 | 23 | 5,429 | 0 | 20 | 5,334 | 0 | 0 | 29 |
| Flammable liquid ^a | 5 | 211 | 3,076 | 5 | 188 | 2,763 | 0 | 19 | 224 |
| Paint remover | 0 | 60 | 2,828 | 0 | 59 | 2,781 | 0 | 1 | 17 |
| Sulfuric acid | 2 | 422 | 2,218 | 2 | 212 | 1,555 | 0 | 210 | 639 |
| Hydrochloric acid | 0 | 104 | 1,760 | 0 | 76 | 1,502 | 0 | 28 | 237 |
| Electrolyte battery fluid | 0 | 5 | 1,310 | 0 | 5 | 1,273 | 0 | 0 | 17 |
| Plastic and resin solutions | 0 | 12 | 1,206 | 0 | 11 | 1,138 | 0 | 0 | 30 |
| Flammable or poisonous insecticides | 0 | 28 | 894 | 0 | 25 | 876 | 0 | 3 | 13 |
| Ink | 1 | 0 | 829 | 1 | 0 | 819 | 0 | 0 | 3 |
| Alcohol ^a | 0 | 13 | 760 | 0 | 8 | 626 | 0 | 4 | 92 |
| Phosphoric acid | 0 | 32 | 671 | 0 | 11 | 278 | 0 | 21 | 384 |
| Sodium hydroxide | 2 | 178 | 635 | 2 | 120 | 451 | 0 | 54 | 173 |
| Acids ^a | 1 | 79 | 573 | 1 | 35 | 537 | 0 | 44 | 25 |
| Anhydrous ammonia | 13 | 404 | 470 | 12 | 265 | 129 | 1 | 139 | 336 |
| Nitric acid | 4 | 82 | 437 | 1 | 76 | 395 | 0 | 2 | 31 |
| Solvents ^a | 0 | 4 | 374 | 0 | 4 | 349 | 0 | 0 | 13 |
| Corrosive solids ^a | 0 | 58 | 370 | 0 | 28 | 350 | 0 | 0 | 15 |
| Compressed gases ^a | 2 | 62 | 512 | 2 | 61 | 465 | 0 | 1 | 28 |
| Radioactive materials | 0 | 2 | 377 | 0 | 0 | 262 | 0 | 0 | 7 |
| Methanol | 0 | 10 | 350 | 0 | 7 | 236 | 0 | 3 | 106 |
| Rust preventers and removers | 0 | 1 | 266 | 0 | 1 | 265 | 0 | 0 | 0 |
| Acetone | 0 | 4 | 219 | 0 | 0 | 171 | 0 | 3 | 38 |
| Xylene | 1 | 7 | 216 | 1 | 3 | 178 | 0 | 0 | 29 |
| Subtotal | 43 | 2133 | 47,043 | 37 | 1504 | 43,468 | 3 | 567 | 2778 |
| All other hazardous materials | 168 | 3180 | 22,988 | 128 | 1740 | 19,790 | 39 | 1264 | 2671 |
| TOTAL | 211 | 5313 | 70,031 | 165 | 3244 | 63,258 | 42 | 1831 | 5449 |

^a Not otherwise specified. Note: Data are for reported incidents, 1971-78. Source: Department of Transportation

Figure 42. Compatibility of chemicals with fluorescence and sonic sensing techniques.

Compatibility of chemicals most frequently involved in transportation incidents with fluorescence and sonic sensing techniques. All organic chemicals cited above are compatible.

pertinent to the fluorescence system.)

7. Underwater sonic sensing techniques were shown to have excellent synergistic effects when used with the fluorescence techniques. Both techniques would be excellent when used on a stand-alone basis. Sonic sensing is particularly invaluable in situations in which a need exists to determine the rate of dissipation of oil into the water column. (See Appendices F and J for additional information regarding features and developments pertinent to sonic sensing techniques.)

Figures 43 through 53 discuss developments in sonic sensing and fluorescence techniques. Our group believes that these new techniques represent powerful supplements to oil and hazardous chemical spill recovery and control efforts.



Figure 43. Commencement of fluorescence test.

OHMSETT crewman is shown here applying fine spray of Ciba-Geigy Uvitex OB (1% solution in cellosolve solvent) to diesel oil slick. Treated oil slick was then allowed to stand for about 5 hours before further observation (see Figures 25 and 26).

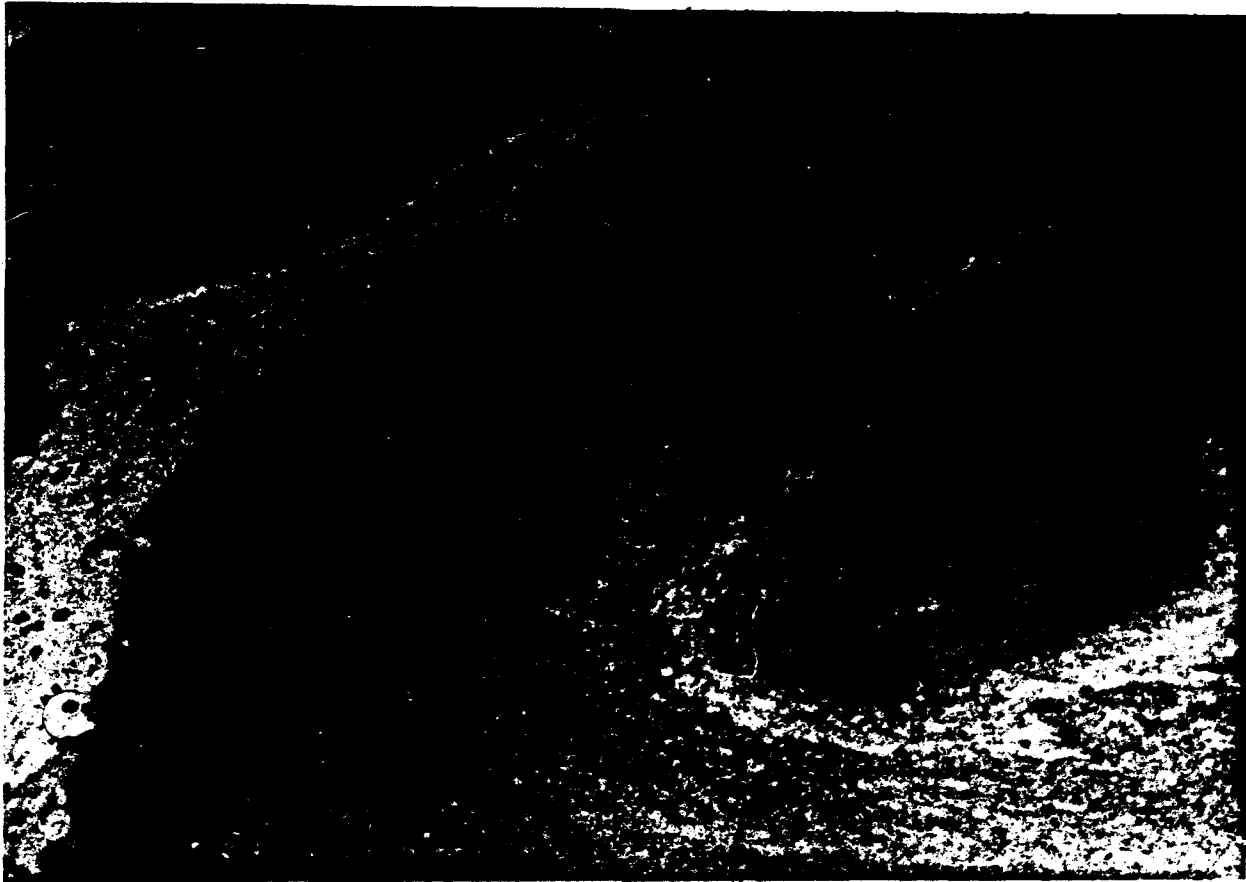
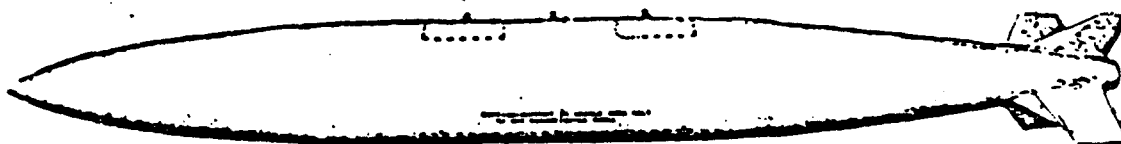


Figure 44. Results of fluorescence test.

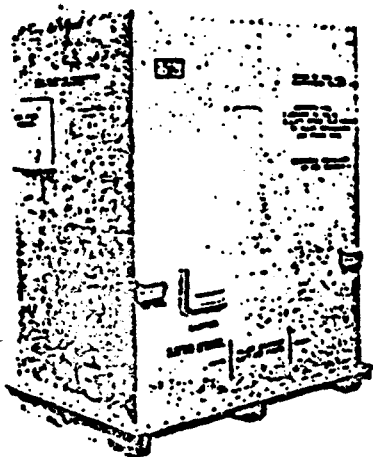
Time: 8:30 PM, August 1, 1979. OHMSETT tank surface illuminated by longwave (366 nm) UV radiation from a battery of four 4-foot fluorescent "black light" UV tubes from the OHMSETT bridge, about 4 feet above the water. That portion of fluorescer which encountered oil patches remained in the oil to the extent that night-time visibility of the oil was readily effected. That portion of the fluorescer which encountered only open water was distributed into the water column, to the extent that fluorescence was imparted only to the oil patches and not to open water areas.

Dimensions: 22" diameter (max.)
 190" length
 660 lb. empty weight
 90 gallon capacity

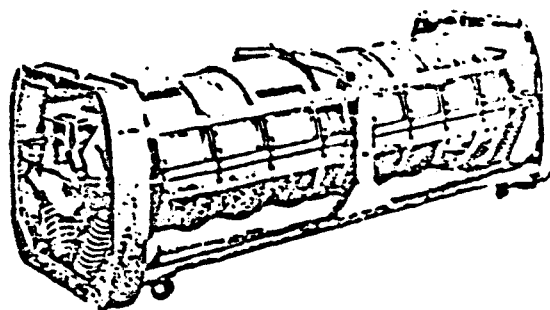
Bomb Lugs
 (30" centers)



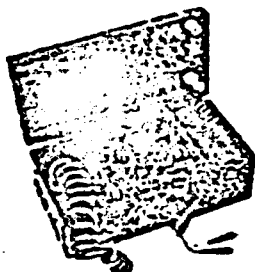
AERO 14B AIRBORNE SPRAY TANK



**AERO 14B COMPONENT
 CONTAINER**



**AERO 14B CENTER SECTION
 CONTAINER**



**AERO 14B SPRAY TANK
 TESTER**



**AERO 14B AIRCRAFT
 WIRING TEST BOX**

Figure 45. EDO Aero 14B airborne spray tank (and auxiliary equipment).

This military equipment is an ideal apparatus for spraying liquid agents and would be particularly well adapted for the fluorescent sprays contemplated for use in this study. It has a capability for heating the liquids in cold weather situations, and provides high accuracy.

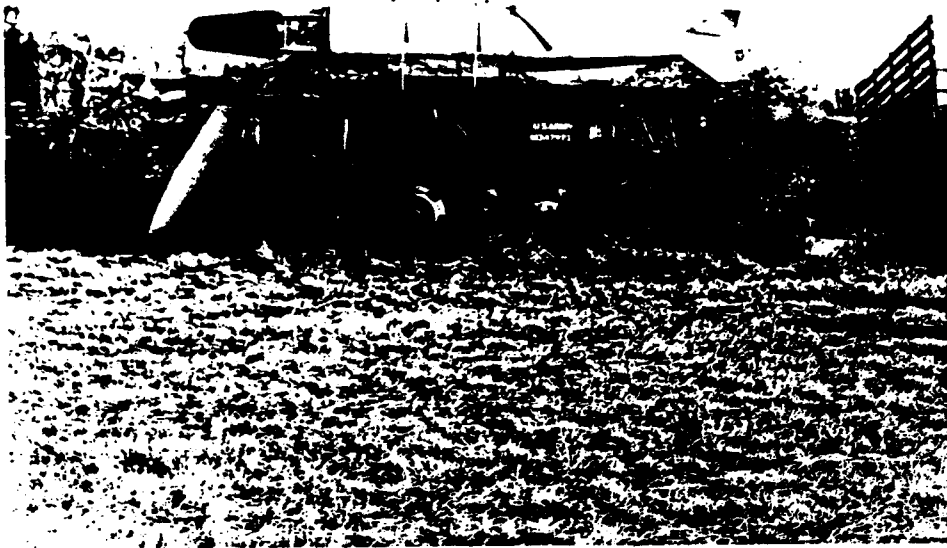


Figure 46. Another view of EDO spray tank.

(The nose cone has been removed for inspection of spray tank controls.)



Figure 47. Commencement of fluorescence dusting test.

80-square-foot test pool immediately after application of 250 ml of mineral oil. Estimated thickness of patches of oil produced was about 0.6 mm.



Figure 48. Dusting with fluorescent powder.

Dusting with fluorescer/ CaSO_4 (2%) formulation to provide estimated 75-ppm concentration of fluorescer in oil.

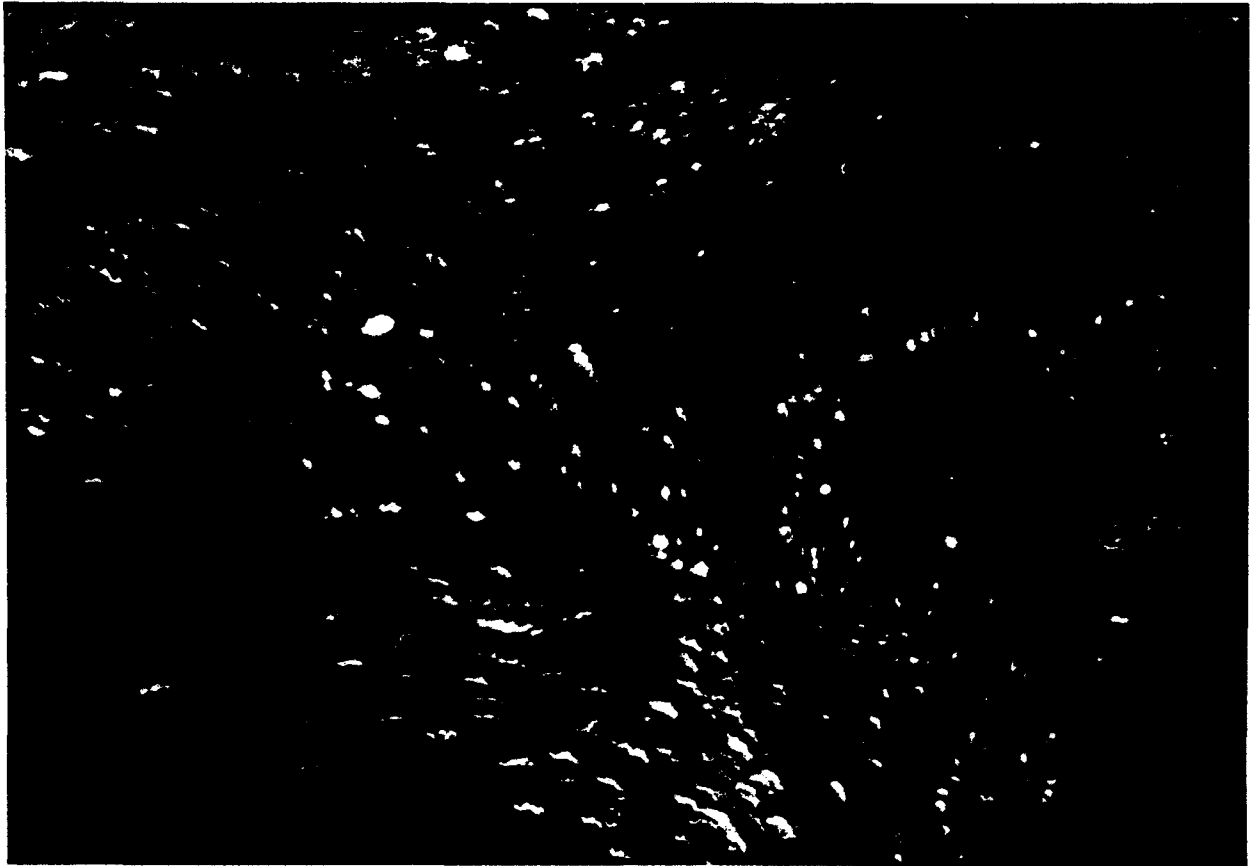


Figure 49. Results of fluorescence test.

Surface of tank, with each patch of oil glowing with yellow fluorescence induced by UV illumination. Fluorescence was much brighter than is indicated in this Polaroid photograph.



Figure 50. Cropdusting by helicopter.

Helicopter delivery of a dry-mix agent (in this case, delivery of fertilizer over Mt. St. Helens area). Similar delivery patterns are observed in aerial spraying operations.

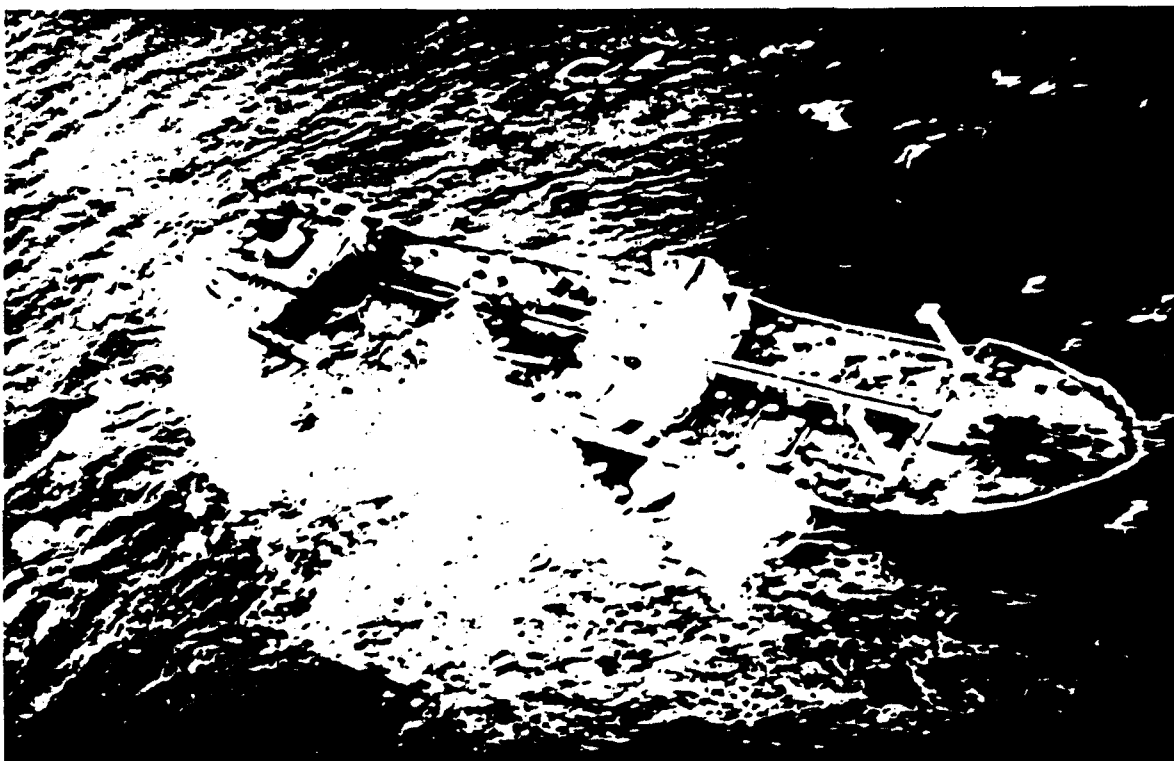


Figure 51. Breakup of ARGO MERCHANT

December 19, 1976 (NOAA/USCG photo)



Figure 52. Oil slick from ARGO MERCHANT

December 19, 1976. Attempts to keep track of, and to predict the course of this spill (as has been the case in many other instances) were severely handicapped by the inability to observe this slick during the long winter night hours. (NOAA/USCG photo)

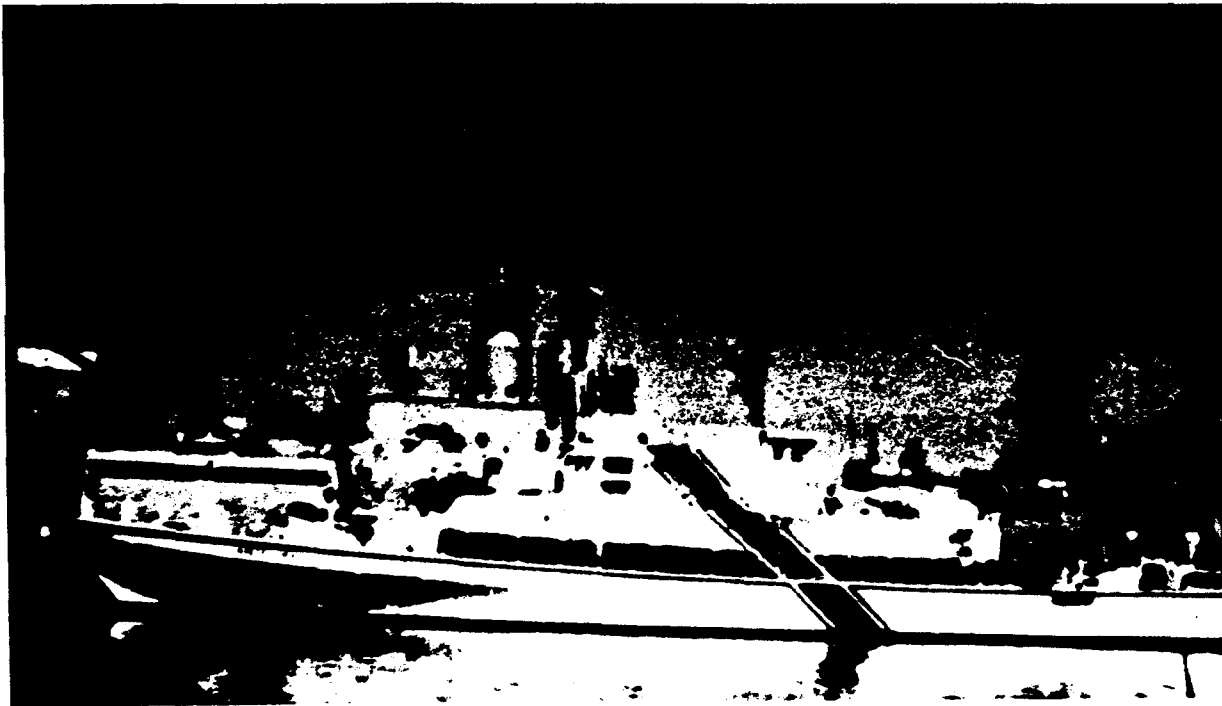


Figure 53. EPA ocean survey vessel ANTELOPE.

EPA OSV ANTELOPE, operating from Annapolis, Maryland. OSV ANTELOPE is utilized by the EPA for environmental research and surveys on inland, coastal, and open waterways. Fluorescence and sonic sensing tests were conducted by this group on board the ANTELOPE in September 1981; future work of this nature is contemplated, again on board the ANTELOPE.

REFERENCES

1. a. Study of Equipment and Methods for Removing Oil Slicks from Harbor Waters. Battelle Memorial Institute, Pacific Northwest Laboratories, Report No. CR-7-001. Prepared under Contract N62399-69-0023 for the Department of the Navy. 1969.
b. Chemical Treatment of Oil Slicks. U.S. Department of Interior, FWPCA, Water Quality Laboratories, Edison, New Jersey. March 1969.
c. Control of Oil and Other Hazardous Materials. Training Manual, U.S. Environmental Protection Agency, Office of Water Programs. September 1972.
d. Chemical and Engineering News. September 7, 1970, p. 48.
e. M.A. Poliakoff. Oil Dispersion Chemicals. Edison Water Quality Laboratories, FWPCA, Edison, New Jersey. 1969.
f. G.P. Canevari. General Dispersant Theory. Proc. Joint Conference on Prevention and Control of Oil Spills. API-FWPCA. December 1969.
g. T. Murphy and L. McCarthy. Evaluating the Effectiveness of Oil Spill Dispersants. *ibid.* 1969.
2. a. JBF Company. U.S. Patents 3,716,142 (1971) and 3,804,251 (1974).
b. Chemical and Engineering News. May 15, 1972. p. 12.
c. References (1) (a,c).
d. Compressed Air Magazine. June 1974. p. 15.
3. a. Proc. Joint Conference on Prevention and Control of Oil Spills. pp. 221 ff.
b. Oil Spill Treating Agents - Test Procedures: Status and Recommendations. Battelle Memorial Institute, Pacific Northwest Laboratories. Prepared under Contract 212B00083 for API. May 1, 1970. pp. 20 ff.
c. Proceedings, Industry Government Seminar. Oil Spill Treating Agents. API/U.S. Department of the Interior. April 8-9, 1970. pp. 95-97.

- d. Oil Spill Treating Agents - Selection Based on Environmental Factors. Battelle Memorial Institute, Pacific Northwest Laboratories. Prepared by A.D. Little Co. for API. October 1970.
- e. Chemical and Engineering News. January 24, 1972. p. 12.
- 4. M.K. Breslin and M.D. Royer. Use of Selected Sorbents and Aqueous Film Forming Foam on Floating Hazardous Materials. EPA-600/52-81-211. U.S. Environmental Protection Agency, Cincinnati, Ohio. October 1981.
- 5. W.W. Bannister, W.A. Curby, and J.A. Pennace. U.S. Patents 3,684,733 (September 18, 1970), and 3,880,569 (April 29, 1975).
- 6. W.W. Bannister. Gelation of Oil Slicks by Amine Carbamates as an Adjunct to U.S. Navy Oil Spill Recovery Operations. Report prepared under Contract N00014-76-C-0340 for the Office of Naval Research. DDC acquisition code 202-274-7633.

W.W. Bannister. New Amine Carbamate Gelation Techniques for Use in Oil Spill Recovery Operations. Report prepared under EPA Project No. R804628 0.

W.W. Bannister, J.D. Rancourt, W.A. Curby, U. Frank, and C. Aguilar. Marine Technology. October 1980. pp. 146-149.
- 7. P.B. Ghosh and M.W. Whitehouse. Biochem. J. 108, 155 (1968).
- 8. U. Frank. U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory, Edison, New Jersey. Private communication.

APPENDIX A

AMINE DTM AND ITS DERIVATIVES BULLETIN OR-132C



BULLETIN OR-132C
(Supersedes PC-132B)

AMINE D, AMINE D ACETATE 70%, AND AMINE D ACETATE 50S

AMINE DTM is a mixture of related primary amines derived from a modified rosin. It can be described chemically as a technical grade of dehydroabietylamine, the dominant amine comprising it. Amine D readily undergoes the usual chemical reactions of primary amines. For use in aqueous systems, it can be converted to the acetic acid salt, which is totally soluble in water. For the convenience of those who may not have facilities to convert to the acetate form, Hercules offers AMINE D ACETATE 70% and AMINE D ACETATE 50S, a 70 percent solids aqueous paste and a 50 percent solids aqueous-alcoholic solution of this salt, respectively.

This bulletin describes typical uses for Amine D and several of its derivatives, and presents detailed information on their physical and chemical properties. Toxicity and handling precautions are also included. Indicated applications include use as surface-active agents, corrosion inhibitors, additives for asphalt, industrial preservatives, chemical intermediates, and flotation reagents. A separate bulletin covers the Polyrad[®] series of ethylene oxide adducts of Amine D. This family of products is especially effective as inhibitors for acid-induced corrosion, particularly for hydrochloric acid.

TYPICAL USES

Asphalt Additives

Amine D and its acetate salt are useful antistripping agents to improve or promote adhesion of asphalts to stone aggregates used in road construction or repair. They are more effective for improving binding of cutback asphalts to siliceous materials than to basic aggregates such as limestone. Generally, 0.5 to 1.25 percent of the amine or amine derivative is required, depending on type of asphalt and aggregate to be coated.

Chemical Intermediates

Amine D is a technical grade of the primary amine dehydroabietylamine, and, as such, is a very reactive chemical. It is used by Hercules and others for manufacture of acetate salts. Many other potentially useful derivatives (see section Chemical Reactivity under Chemical and Physical Properties of Amine D) can be made.

Corrosion Inhibitors

Reaction products of Amine D with ethylene oxide (Polyrad products) are highly effective corrosion inhibitors for hydrochloric acid used in chemical specialties (bowl cleaners), industrial cleaning, and oil well acidizing. These water-soluble inhibitors are especially useful in petroleum refinery streams for reducing corrosion of equipment by hydrogen sulfide, hydrogen chloride, carbon dioxide, and organic acids. In addition, these materials act as detergents in loosening and dispersing scale-forming materials present in refinery systems. Information in greater detail on Polyrad products is available in other Hercules literature.

Flotation Reagents

The acetate of Amine D is an excellent collector for silica and silicate minerals. It is used primarily in the beneficiation of nonmetallic ores such as feldspar, quartz, phosphate rock, and cement rock. It is useful also, alone or in conjunction with other reagents, for the beneficiation of iron oxide and other metallic ores. More detailed information on flotation applications of the acetate salt is available in another Hercules publication.

Preservatives

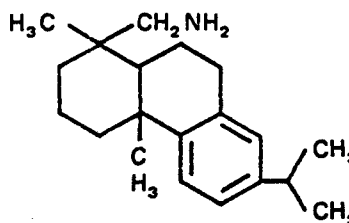
The pentachlorophenol salt of Amine D is a very effective ingredient of preservatives used in emulsion paints; wood-treating compounds; and cordage, felt, fabric, and paper that are not exposed to sunlight. The pentachlorophenate is neither manufactured nor sold by Hercules, but can be readily made by hot fusion of the above materials. A description of this derivative follows.

The pentachlorophenol salt of Amine D, which is sometimes referred to as technical dehydroabietylammmonium pentachlorophenoxide, is a dark amber, brittle, resinous solid. Softening point of a typical sample is 104°C; specific gravity at 20/20°C is 1.288. Vapor pressure of the pentachlorophenate is approximately one-tenth that of pentachlorophenol itself. The pentachlorophenate of Amine D is readily soluble in polar-type solvents such as pine oil, and in various aliphatic and aromatic hydrocarbons.



CHEMICAL AND PHYSICAL PROPERTIES OF AMINE D

Amine D is a mixture of high molecular weight primary amines derived from the resin acid constituents of a modified rosin. They are mainly stabilized abietyl-amines, the predominant one being dehydroabietylamine whose structural configuration is shown at the right. Typically, Amine D contains around 92 percent total amines of which about 3 percent are related secondary amines. It is a clear, yellow, viscous liquid having a faint ammoniacal odor. Other physical and chemical properties are shown below.



Typical Properties of Amine D

| | <u>Amine D</u> |
|----------------------------------|----------------|
| Color, Gardner | 7 |
| Specific gravity at 25/15.6°C | 1.00 |
| Refractive index at 20°C | 1.545 |
| Pounds per gallon at 25°C (kg/l) | 8.3 (1.0) |
| Viscosity, poises at 25°C | 87 |
| Flash point, °F (°C) | 378 (192) |
| Neutralization equivalent | 316 |
| Secondary amine content, % | 3 |
| Total amine content, % | 92 |

Solubility — For all practical considerations, Amine D is insoluble in water. For example, solubility in water is less than 0.5 gram per 100 grams of water at 100°C. However, it is soluble in common organic solvents, including alcohols, ethers, hydrocarbons, and chlorinated solvents. For use in water or with aqueous systems, the amine can be reacted with acetic acid to form a water-soluble salt. Hercules offers the acetate salt of Amine D as a convenience to users who prefer to purchase rather than make the salt themselves.

Stability to Heat and Storage — Amine D is quite stable to heat below 100°C. Above this temperature, gradual decomposition occurs and increases as the heating time and temperature are increased. This is illustrated by the following data, on page 4, obtained on a typical sample of Amine D.

| Time of Heating (days) | Temperature, °C | Weight Loss of Amine D During Heating, % |
|---------------------------|--------------------|---|
| 1 | 100 | 1.1 |
| 3 | 100 | 2.2 |
| 7 | 100 | 3.2 |
| 1 | 150 | 10.5 |
| 3 | 150 | 18.0 |
| 7 | 150 | 35.4 |
| 7.5 hours | 203 | 14.9 |

The viscosity of Amine D decreases sharply with increase in temperature. When cold it is very viscous, but on warming it becomes sufficiently fluid to pump or otherwise transfer without difficulty.

Most metals are unaffected by Amine D under normal conditions of contact and storage. Laboratory tests showed no effect on black iron, stainless steel, Monel, copper, nickel, tin, zinc, or aluminum at room temperature. At 300°F (149°C), Amine D caused slight corrosion (approximately 2 mils per year) of black iron, Monel, nickel, tin, and zinc, but had no effect on stainless steel, aluminum, or copper.

Surface Activity — Amine D facilitates the wetting of siliceous surfaces, as illustrated by the contact angle measurement data that follow:

| Test Sample | Contact Angle Against Glass Immersed in Water (average value) |
|--------------------------------|--|
| Mineral spirits alone | 131° |
| Mineral spirits + 0.1% Amine D | 114° |
| Mineral spirits + 1.0% Amine D | 96° |
| Mineral spirits + 5.0% Amine D | 77° |

These tests were made by releasing drops of solution of Amine D in mineral spirits beneath glass plates submerged in water, in a horizontal position, and measuring the contact angle directly with a microscope. The smaller the angle, the greater the wetting.

Chemical Reactivity — Amine D offers manufacturing chemists an unusual, high-purity, high molecular weight amine. As a chemical raw material or intermediate, it may be considered to be a technical grade of dehydroabietylamine, a condensed-ring-structure, partially aromatic primary amine whose structure is shown on page 3. It undergoes the many and varied reactions commonly associated with amines of this type. A few examples are its reaction with acids to produce amine salts, with alkyl halides to produce secondary and tertiary amines and amides, and with anhydrides to form imides. On the following two pages, in equation form, are other potential chemical reactions to which Amine D can be applied.

Particularly valuable derivatives of Amine D are the simple salts formed by reaction with carboxylic acids and acidic phenols. Examples are the salts of acetic acid and pentachlorophenol. The commercially available acetates of Amine D are discussed on page 7.



OR-132C

Possible Chemical Reactions of AMINE D (RNH₂)

| Product: | From Reaction of RNH ₂ With: | According to These Equations: |
|--|---|--|
| AMINE SALTS | a. Mineral Acids | $\text{RNH}_2 + \text{HCl} \rightarrow [\text{RNH}_2]^+ \text{Cl}^-$ $2 \text{RNH}_2 + \text{H}_2\text{SO}_4 \rightarrow [2\text{RNH}_2]^{++} [\text{SO}_4]^{--}$ |
| | b. Carboxylic or Sulfonic Acids | $\text{RNH}_2 + \text{CH}_3\text{COOH} \rightarrow [\text{RNH}_2]^+ [\text{CH}_3\text{COO}]^-$ <p style="text-align: center;">acetic acid Amine • acetate</p> $\text{RNH}_2 + p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H} \rightarrow [\text{RNH}_2]^+ [p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3]^-$ <p style="text-align: center;">p-toluenesulfonic acid</p> |
| | c. Strongly Acidic Phenols | $\text{RNH}_2 + \text{Cl}_3\text{C}_6\text{H}_2\text{OH} \rightarrow [\text{RNH}_2]^+ [\text{Cl}_3\text{C}_6\text{H}_2\text{O}]^-$ <p style="text-align: center;">penta-chlorophenol Amine • pentachlorophenolate</p> |
| N-SUBSTITUTED AMINES (1) Secondary Amines | a. Alkyl or Aryl Halides | $\text{RNH}_2 + \text{CH}_3\text{I} \rightarrow [\text{RNH}_2\text{CH}_3]^+ \text{I}^-$ <p style="text-align: center;">methyl monoamine salt iodide</p> $\text{RNH}_2 + \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \rightarrow [\text{RNH}_2(\text{C}_6\text{H}_5\text{CH}_2)]^+ \text{Cl}^-$ <p style="text-align: center;">benzyl monoamine salt chloride</p> |
| | b. Alkene Halides | $2 \text{RNH}_2 + \text{ClCH}_2\text{CH}_2\text{Cl} \rightarrow [\text{RNH}_2\text{CH}_2\text{CH}_2\text{NR}]^{++} [2\text{Cl}]^{--}$ <p style="text-align: center;">ethylene diamine salt chloride</p> |
| | c. Olefins | $\text{RNH}_2 + \text{CH}_2=\text{CHCH}_3 \rightarrow \text{RNHCH}(\text{CH}_3)_2$ <p style="text-align: center;">propene</p> |
| (2) Tertiary Amines | a. Alkyl Halides | $\text{RNH}_2 + 2 \text{CH}_3\text{I} \rightarrow [\text{RNH}(\text{CH}_3)_2]^+ \text{I}^- + \text{HI}$ |
| | b. Formaldehyde plus Formic Acid | $\text{RNH}_2 + 2 \text{HCHO} + 2 \text{HCOOH} \rightarrow \text{RN}(\text{CH}_2)_2 + 2 \text{CO}_2 + 2 \text{H}_2\text{O}$ |
| (3) Quaternary Salts | Alkyl Halides | $\text{RNH}_2 + 3 \text{CH}_3\text{I} \rightarrow [\text{RN}(\text{CH}_3)_3]^+ \text{I}^- + 2 \text{HI}$ |
| (4) N-Methylolamine | Formaldehyde | $\text{RNH}_2 + \text{HCHO} \rightarrow \text{RNHCH}_2\text{OH}$ |
| (5) N-Hydroxyethylated Amines | Ethylene Oxide | $\text{RNH}_2 + \text{H}_2\text{C} \begin{array}{c} \text{---} \text{CH}_2 \\ \text{O} \end{array} \rightarrow \text{RNHCH}_2\text{CH}_2\text{OH}$ <p style="text-align: center;">N-hydroxyethyl Amine •</p> $\text{RNH}_2 + 2 \text{H}_2\text{C} \begin{array}{c} \text{---} \text{CH}_2 \\ \text{O} \end{array} \rightarrow \text{RN}(\text{CH}_2\text{CH}_2\text{OH})_2$ <p style="text-align: center;">N, N-bis(hydroxyethyl) Amine •</p> $\text{RNH}_2 + n \text{H}_2\text{C} \begin{array}{c} \text{---} \text{CH}_2 \\ \text{O} \end{array} \rightarrow \text{RN}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{OH}$ <p style="text-align: center;">N, N-bis(hydroxypolyethoxyethyl) Amine •</p> |
| | | |
| | | |
| (6) N-Carboxalkylated Amines | a. alpha-Chloro Acids | $\text{RNH}_2 + \text{ClCH}_2\text{COOH} + 2 \text{NaOH} \rightarrow \text{RNHCH}_2\text{COONa} + \text{NaCl} + 2 \text{H}_2\text{O}$ |
| | b. beta-Propiolactone | $\text{RNH}_2 + \text{CH}_3\text{CH}_2\text{C} \begin{array}{c} \text{---} \text{O} \\ \text{O} \end{array} \rightarrow \text{RNHCH}_2\text{CH}_2\text{COOH}$ <p style="text-align: center;">N-substituted beta-alanine</p> |
| (7) N-Sulfoalkylated Amines | Halosulfonic Acids | $\text{RNH}_2 + \text{BrCH}_2\text{CH}_2\text{SO}_3\text{H} + 2 \text{NaOH} \rightarrow \text{RNHCH}_2\text{CH}_2\text{SO}_3\text{Na} + \text{NaBr} + 2 \text{H}_2\text{O}$ <p style="text-align: center;">2-bromoethyl-sulfonic acid</p> |
| (8) N-Cyanoalkylated Amines | Acrylonitrile | $\text{RNH}_2 + \text{CH}_2=\text{CHCN} \rightarrow \text{RNHCH}_2\text{CH}_2\text{CN}$ |
| ISOCYANATES | Phosgene | $\text{RNH}_2 + \text{HCl} + \text{COCl}_2 \rightarrow \text{RNCO} + 3 \text{HCl}$ <p style="text-align: center;">*AMINE D.</p> |

Possible Chemical Reactions of AMINE D (RNH₂)

| Product: | From Reaction of RNH ₂ With: | According to These Equations: |
|--|--|---|
| AMIDES AND IMIDES | a. Anhydrides of (1) Monocarboxylic Acids (2) Dicarboxylic Acids | $\text{RNH}_2 + (\text{CH}_3\text{CO})_2\text{O} \rightarrow \text{CH}_3\text{CONHR} + \text{CH}_3\text{COOH}$ <p style="text-align: center;">acetic anhydride</p> $\text{RNH}_2 + \text{O}-\text{CCH}=\text{CHC}-\text{O} \rightarrow \text{RNHCCH}=\text{CHCOOH}$ <p style="text-align: center;">maleic anhydride $\xrightarrow{\text{heat}}$ $\text{O}-\text{CCH}=\text{CHC}-\text{O} + \text{H}_2\text{O}$ imide NR</p> $\text{RNH}_2 + \text{O}-\text{CC}_6\text{H}_4\text{C}-\text{O} \rightarrow \text{O}-\text{CC}_6\text{H}_4\text{C}-\text{O} + \text{H}_2\text{O}$ <p style="text-align: center;">phthalic anhydride imide NR</p> |
| | b. Acyl Halides | $\text{RNH}_2 + \text{CH}_3\text{COCl} \rightarrow \text{CH}_3\text{CONHR} + \text{HCl}$ <p style="text-align: center;">acetyl chloride</p> $\text{RNH}_2 + \text{C}_6\text{H}_5\text{SO}_2\text{Cl} \rightarrow \text{C}_6\text{H}_5\text{SO}_2\text{NHR} + \text{HCl}$ <p style="text-align: center;">benzene-sulfonyl chloride sulfonamide</p> |
| | c. Diethyl Oxalate | $\text{RNH}_2 + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{RNHCOCOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH}$ <p style="text-align: center;">monoamide</p> |
| N-SUBSTITUTED UREAS | a. Potassium Cyanate | $\text{RNH}_2 + \text{KCNO} + \text{HCl} \rightarrow \text{RNHCONH}_2 + \text{KCl}$ |
| | b. Isocyanates | $\text{RNH}_2 + \text{R}'\text{NCO} \rightarrow \text{RNHCONHR}'$ <p style="text-align: center;">(R' = alkyl or aryl)</p> |
| | c. Urea | $\text{RNH}_2 + \text{H}_2\text{NCONH}_2 \rightarrow \text{RNHCONH}_2 + \text{NH}_3$ $2 \text{RNH}_2 + \text{H}_2\text{NCONH}_2 \rightarrow \text{RNHCONHR} + 2 \text{NH}_3$ |
| N-SUBSTITUTED THIOUREAS | Carbon Disulfide | $2 \text{RNH}_2 + \text{CS}_2 \xrightarrow{\text{heat}} [\text{RNH}_2]^+ [\text{RNHCS}]^-$ <p style="text-align: center;">$\xrightarrow{\text{heat}}$ RNHCSNHR - H₂S N, N'-disubstituted thioureas</p> |
| CHLORAMINE | Hypochlorous Acid | $\text{RNH}_2 + \text{HOCl} \rightarrow \text{RNHCl} + \text{H}_2\text{O}$ |
| METAL COORDINATION COMPOUNDS OR AMINES | Metal Salts: acetates, sulfates, nitrates, and chlorides of Cu, Zn, Ag, Ni, Mn, Co, Hg, Ca, Fe, Al, and Cr | $2 \text{RNH}_2 + (\text{CH}_3\text{COO})_2\text{Cu} \rightarrow [\text{Cu}(\text{RNH}_2)_2](\text{CH}_3\text{COO})_2$ $2 \text{RNH}_2 + \text{ZnCl}_2 \rightarrow [\text{Zn}(\text{RNH}_2)_2]\text{Cl}_2$ |
| PHOSPHONIUM COMPOUNDS | Phosphoryl Chloride | $\text{RNH}_2 + \text{POCl}_3 \rightarrow \text{RNHPOCl}_2 + \text{HCl}$ $\text{RNHPOCl}_2 + \text{RNH}_2 \rightarrow (\text{RNH})_2\text{POCl} + \text{HCl}$ $(\text{RNH})_2\text{POCl} + \text{RNH}_2 \rightarrow (\text{RNH})_3\text{PO} + \text{HCl}$ |
| SCHIFF'S BASES | a. Aldehydes | $\text{RNH}_2 + \text{C}_6\text{H}_5\text{CHO} \rightarrow \text{RN}=\text{CHC}_6\text{H}_5 + \text{H}_2\text{O}$ <p style="text-align: center;">benz-aldehyde</p> |
| | b. Ketones | $\text{RNH}_2 + (\text{C}_6\text{H}_5)_2\text{CO} \rightarrow \text{RN}=\text{C}(\text{C}_6\text{H}_5)_2 + \text{H}_2\text{O}$ <p style="text-align: center;">benzo-phenone</p> |
| ISONITRILES | Chloroform | $\text{RNH}_2 + \text{CHCl}_3 + 3 \text{KOH} \xrightarrow{\text{alcohol}} \text{RNC} + 3 \text{KCl} + 3 \text{H}_2\text{O}$ |
| | | |



OR-132C

CHEMICAL AND PHYSICAL PROPERTIES OF AMINE D ACETATE

The acetic acid salt of Amine D is commercially available from Hercules as Amine D Acetate. Two concentrations are offered: a 70 percent solids aqueous paste and a 50 percent solids aqueous-alcoholic solution. Properties of these products are shown below:

Properties of Amine D Acetate

| | Amine D Acetate | |
|-------------------------------------|-----------------|--------------|
| | 70% | 50S |
| Solids content, % | 70 | 50 |
| Water content, % | 30 | 39 |
| Isopropyl alcohol content, % | — | 11 |
| Specific gravity at 25/15.6°C | 1.036 | 1.017 |
| Pounds per gallon at 25°C (kg/l) | 8.630 (1.04) | 8.460 (1.02) |
| Viscosity at 25°C, poises | solid paste | 1.070 |
| Flash point, Tag. open cup, °F (°C) | — | 140 (60) |
| Freezing point, °F (°C) | — | 15 (-9) |

Solubility — Amine D Acetate is quite soluble in water and lower molecular weight alcohols. Its solubility in most other organic solvents is not as great. In very hard waters, the presence of ions such as phosphate, chloride, and sulfate causes cloudy solutions. In waters of normal hardness, dilute solutions of the acetate (0.01 to 1 percent) may frequently be hazy, but higher strength solutions of from 1 to 50 percent are generally clear. Fifty percent concentrations are about the limit of solubility of the acetate in water at room temperature.

NOTE: The 50 percent solids commercial form of this acetate is readily diluted with water to lower concentrations. The most satisfactory dilution procedure for the 70 percent solids product, which is a heavy paste, is as follows: (1) add 1 part of water to 1 part of the paste and stir until mixture is uniform; (2) let stand 24 hours, after which the fluid paste can be readily diluted to any desired lower concentration.

Stability to Heat and Storage — The water- and alcohol-free acetate of Amine D is stable to heat below temperatures of around 90°C. Upon prolonged heating at higher temperatures, it is converted into the free amine and acetic acid, or to an N-substituted acetamide when the acetic acid formed cannot readily escape. For example, in a closed system, when a sample of the acetate of Amine D (100 percent solids) was heated 65 hours at 65°C, no change in composition occurred; when heated at 165°C for 1.5 hours, this salt was converted completely to an acetamide.

Stability to Air and Sunlight – A characteristic of high molecular weight primary amines and their salts is susceptibility to oxidation when thin films on various substrates are exposed to air in the presence of sunlight. Sunlight catalyzes the oxidation. In the absence of sunlight, oxidation is negligible. The acetate of Amine D, being a high molecular weight primary amine salt, also has this characteristic.

Surface Activity – The acetate of Amine D has definite surfactant properties. It shows marked wetting activity on siliceous surfaces. In aqueous solution, Amine D Acetate is adsorbed by cellulose fibers, threads, and fabrics, and, after drying, is not readily removed by subsequent washing. Also, the wetting time of cotton, as measured by the Draves method, is markedly decreased by the presence of small amounts of this salt in the water.

The following data illustrate these wetting properties, and show how surface tension and interfacial tension between water and organic liquids are decreased by the presence of this acetate:

| Amine D Acetate (concentration in water, %) | 0 | 0.01 | 0.10 | 0.15 | 0.175 | 0.20 | 0.50 | 1.00 |
|---|------|------|------|------|-------|------|------|------|
| Surface tension, dynes/cm at 25°C | 72.1 | 55.4 | 37.7 | – | – | 33.4 | 33.4 | – |
| Interfacial tension (isooctane-water), dynes/cm at 25°C | 47.5 | – | 9.2 | – | – | – | – | 0.9 |
| Wetting speed, Draves method (cotton), sec | – | – | 180 | 50 | 18 | 9 | – | – |

TOXICITY AND HANDLING PRECAUTIONS

Like most amines and their salts, Amine D and the acetate, although of relatively low toxicity, should be handled with care. These products may cause skin irritation. Avoid prolonged or repeated contact with the skin.

Dermatological studies indicate that Amine D and certain of its derivatives are not skin sensitizers. At concentrations below 0.5 percent, they do not act as primary irritants even on prolonged exposure to the skin. However, concentrated solutions or the undiluted material on prolonged exposure do act as primary skin irritants, just as do many other amines and their salts.

If accidental contact is made with the skin, wipe off at once. In the case of Amine D, apply vinegar or a 5 percent solution of acetic acid and follow with thorough washing, using mild soap and water. The acetate salt form should be removed promptly by first washing with water followed by thorough washing with mild soap and water.

Should these products contact the eyes, immediately flush with plenty of water for at least 15 minutes; get medical attention. If spilled on clothing, remove and wash before reuse.

APPENDIX B

TOXICITY OF HERCULES AMINE D TO MARINE LIFE

In an attempt to determine the nature of the toxic substance or substances in Amine-D and #2 fuel oil mix, several experiments were conducted. Using the barrier tank apparatus described in our previous report (see attached), one ml aliquots of #2 fuel oil with 3% ethanol added were mixed with artificial seawater to make up one liter final volume. Any one of five Fundulus heteroclitus taken from the holding tank was checked at random for normalcy and the other four were placed in the test tank. At the end of two hours, the fish were sacrificed, and blood from the caudal artery was analyzed electronically. Standard slides for microscopic evaluation were also made. Differential blood counts and photomicrographic images were prepared from each slide. Figure (A) shows a photomicrograph taken of a blood slide from a control sample fish (swimming in a barrier tank in one liter of artificial seawater). Figure (B) shows the change in the blood cell population of F. heteroclitus subjected to 970ppm of #2 fuel oil in artificial seawater for 2 hours. Our previous work showed that F. heteroclitus specimens were able to withstand 5-10ppm of Hercules Amine-D (solubilized with 3% ethanol) in artificial seawater for 24 hours without exhibiting any untoward reactions, and that they

could withstand the mix of the Amine-D, ethanol and #2 fuel oil in low concentrations 10-20ppm in artificial seawater for 24 hours. In this latter case, however, the electronic monitoring showed that the blood cells had been altered. In our final experiments, therefore, we stressed the system and looked at the acute toxic effects of the Amine-D/ethanol and the Amine-D/ethanol plus #2 fuel oil mix in 688ppm concentration respectively.

Differential blood counts done on all samples showed that the erythrocyte: lymphocyte: thrombocyte: granulocyte ratios did not change significantly. The electronic patterns and the optical microscope observations showed that the erythrocytes were effected, moreover, fish on both sides of the barrier which keeps the insoluble chemicals available to only one half of the fish in the sample were effected similarly, thus indicating that the toxic chemical or chemicals are seawater soluble.

Table 1 summarizes the survival data and the chemical insults that test populations of F. heteroclitus were subjected to. Amine-D was added directly to the blood of F. heteroclitus as a second type of control. Amounts of Amine-D in saline ranging from 33ppm to full strength were used. All blood cells were altered regardless of the concentration, however, the effect was similar to the results seen in Figure (B), viz. an elongation of the blood cells with little or no cell membrane damage.

Acute toxic reaction in fish swimming in artificial sea-

water containing ethanol, Amine-D alone or in combination with #2 fuel oil effected the blood cell membrane in a manner similar to that seen in chronic copper (II) toxic reactions. The surface of the membrane loses its selective permeability and spots appear fairly evenly distributed over the cell surface. A difference between the two reactions does exist. In the case of the Amine-D reaction, the ratios of the formed elements in the blood do not appear to change. This indicates that the mechanism of action is different from that seen in F. heteroclitus subjected to copper (II) ions. The lethal interval also is interesting for Amine-D toxicity because it suggests (when combined with earlier data) that the soluble toxin is in the Amine-D and may be a contaminant. We have a minimum of information sufficient to relate the lethal interval to the Amine-D concentration regardless of whether the amine is combined in a gel, in a free mix with #2 fuel oil or solubilized in a small amount of ethanol follows a relationship which can be predicted from Graph (1). Amine-D concentrations of less than 20ppm appear to be able to be handled by the fish as easily as the fuel oil itself and, in fact, cause alterations in the blood similar to that seen in Figure (B).

If, as we conclude from the data, it is a soluble contaminant in the Amine-D that is causing the observed toxic response, then further testing will prove the fact. Regardless of the toxin, however, in Amine-D concentration levels of 20ppm or less can be accepted as safe. The concentrations

of Amine-D used to incorporate into an oil spill at sea will be mixed with a volume of water sufficient to lower the concentration of the toxin to a safe level at less than 2 feet below the seawater surface even under the condition of no mixing.



Fig. A. Normal red blood cells show the characteristic elliptical shape and smooth, rigid membrane. Nuclei in these cells are not as clearly defined as those in the experimental cells.



Fig. B. Red blood cells from fish exposed to the oil/EtOH mixture show large deviations in cell width, with most cells being much narrower than normal.

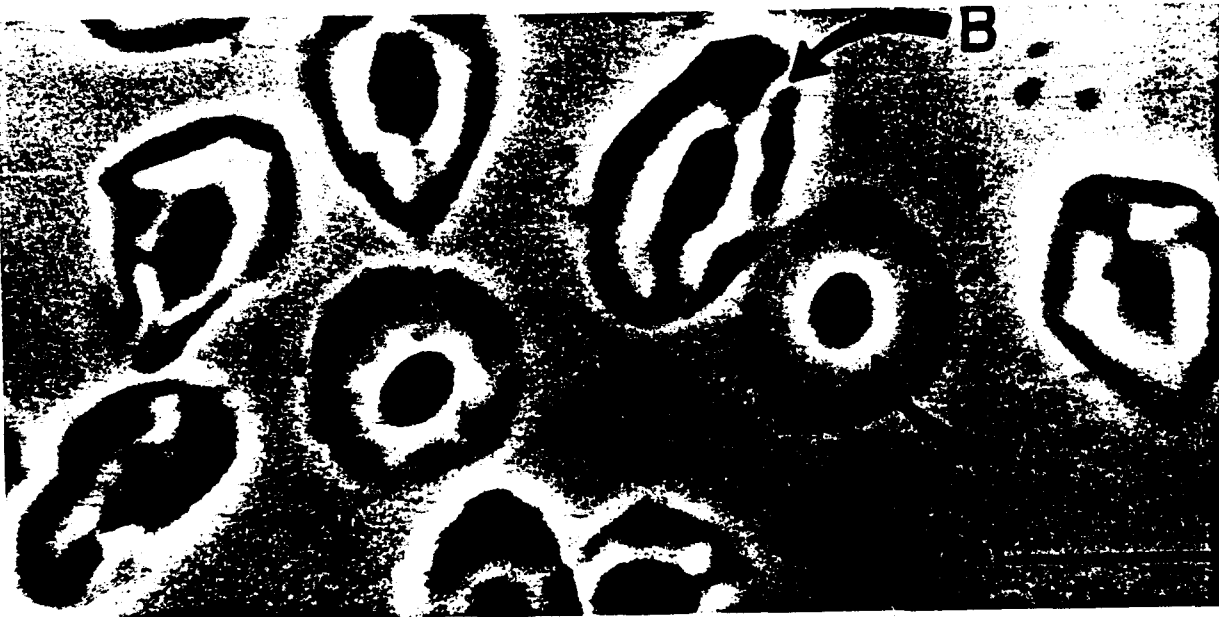


Fig. C. Nuclei appear to project from the cells (A) and shedding of the cytoplasm (B) is evident.



Fig. D. Isolated nuclei (A) of red blood cells; some cells show a loss of cytoplasm exhibited by clearing rings (B) around nuclei.



Fig. E. Cytoplasmic membranes show breaks and loss of rigidity (A) in RBC's from the oil/Amine D/EtOH experiments.

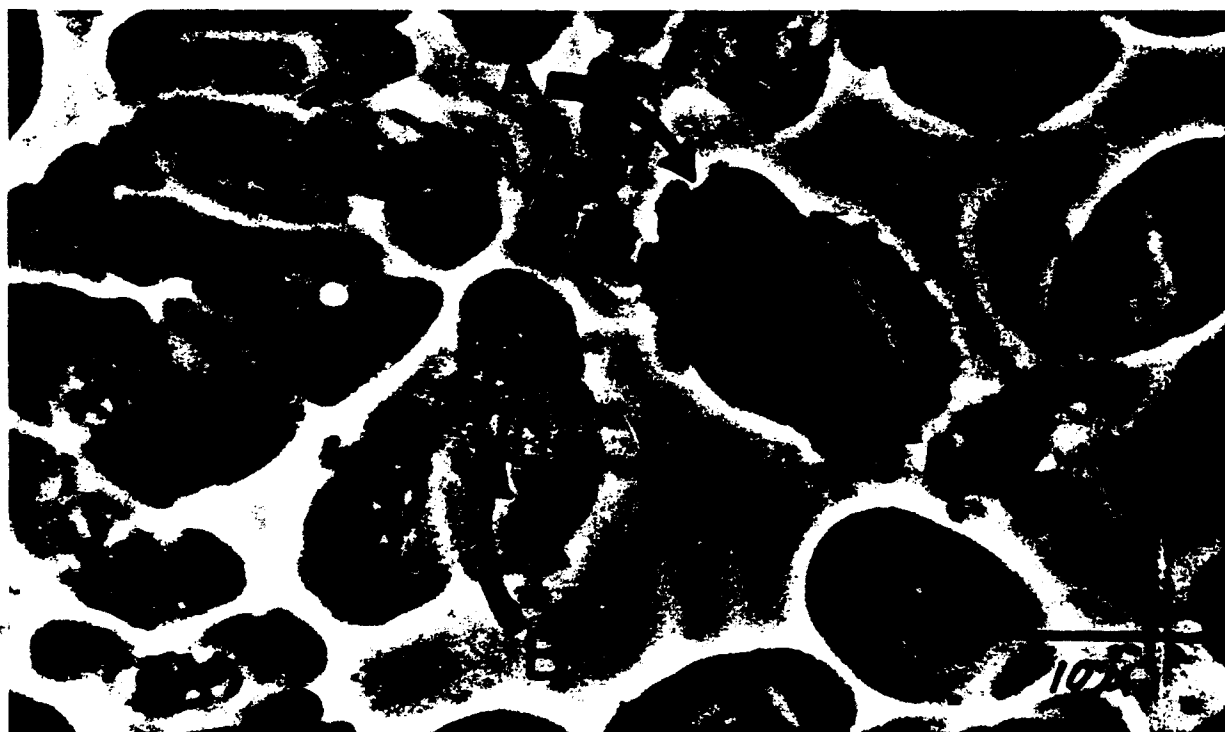


Fig. F. Red blood cells from fish exposed to amine-D/EtOH show a loss of rigidity of the cytoplasmic (A) and nuclear (B) membranes. Folds and projections of the membrane resemble pseudopods (C).

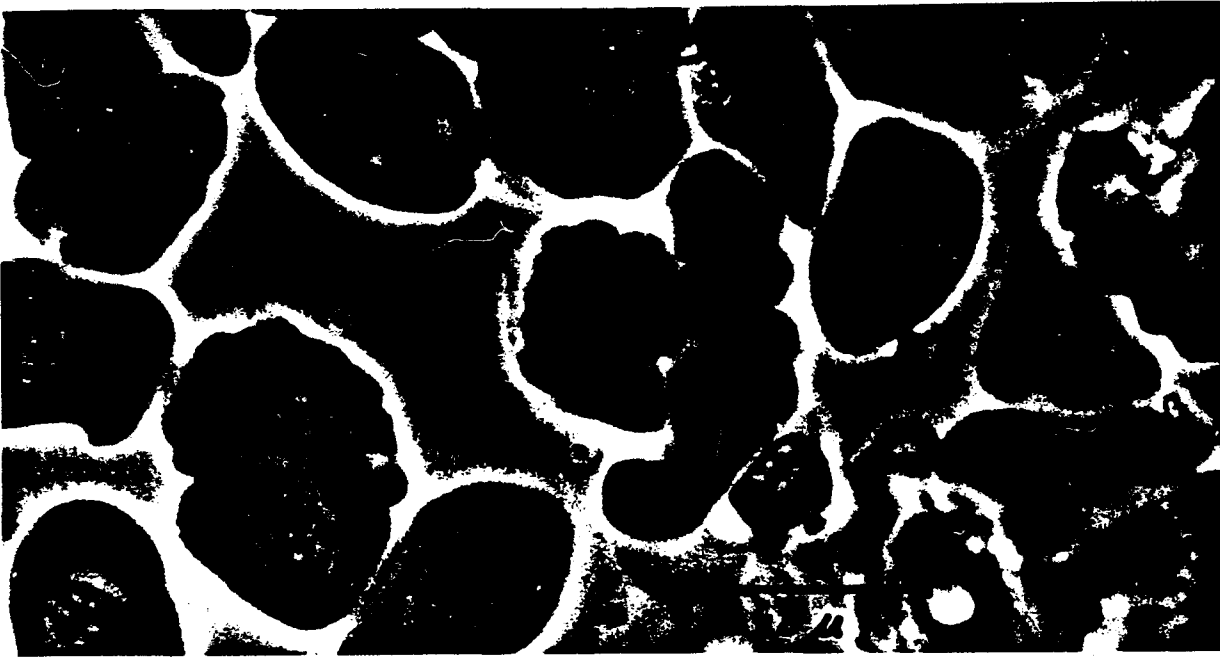


Fig. G. Cytoplasmic membranes take on a scallop shape as the projections begin to develop.

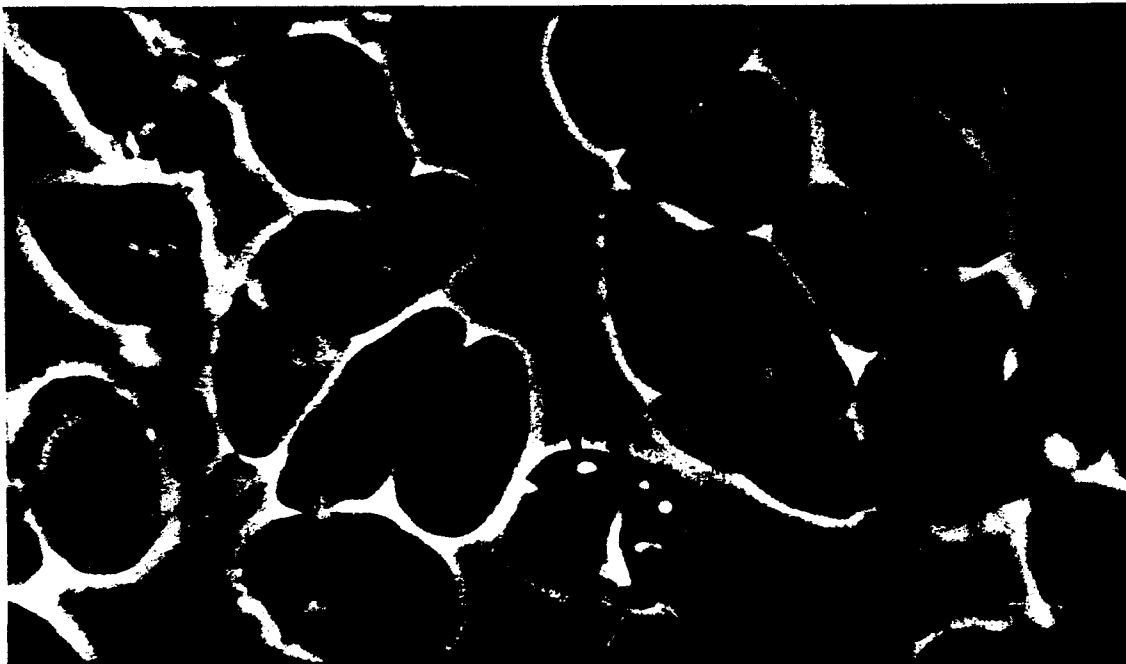
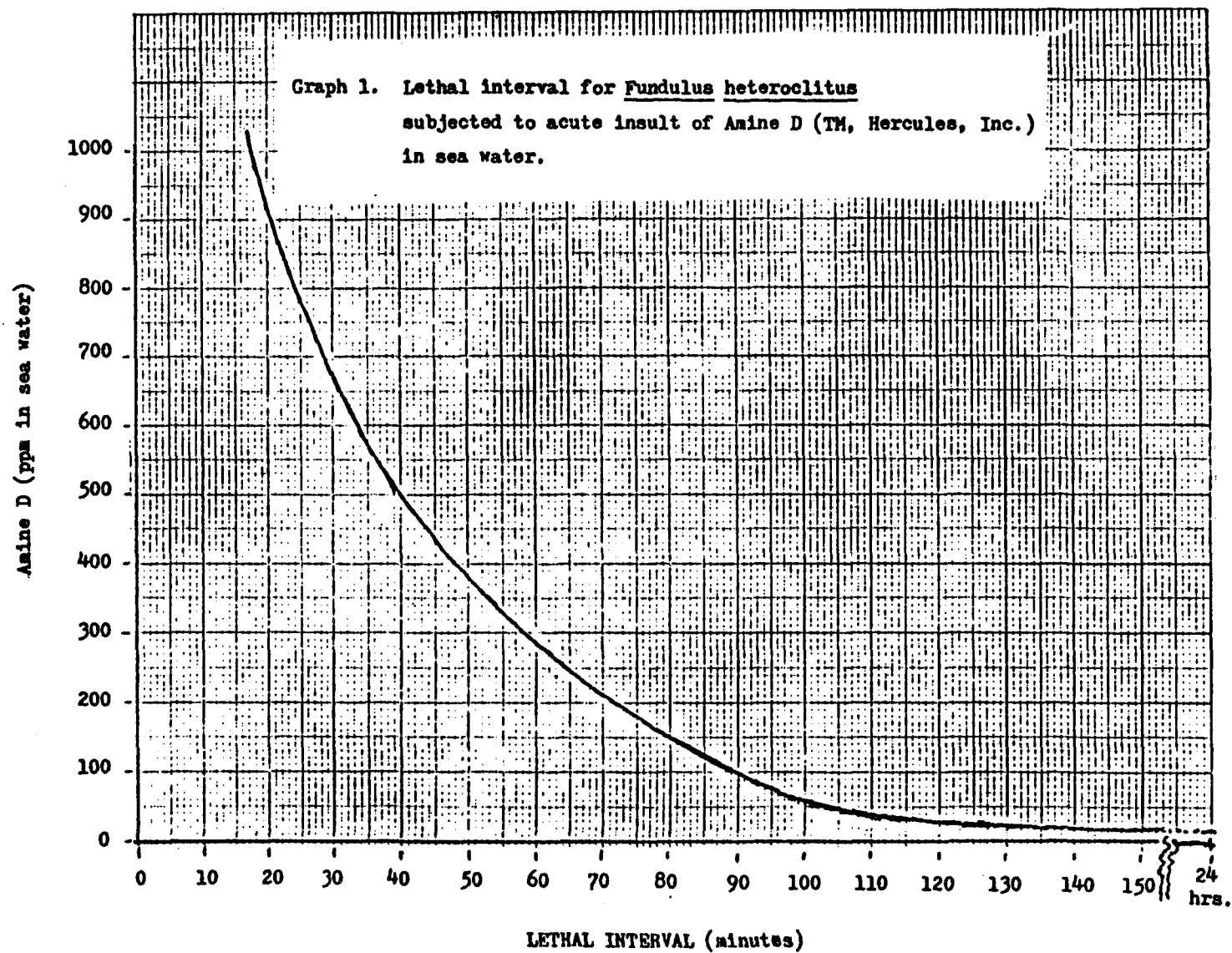


Fig. H. Vacuoles or engulfed particles appear (A), possibly taken in by pseudopodic action.

TABLE I

| Reference Figure | Lethal Application (min.) | TEST ENVIRONMENT | | | | RANDOM 300 COUNT OF BLOOD SAMPLES | | | |
|---------------------|---------------------------------|--------------------------------|------------------------------|-----------------------------|-----------------|-----------------------------------|------------|-------------|-------------|
| | | Artificial Seawater (ml) | Number 2 Fuel Oil (ml) | Hercules Amine-D (ml) | Ethanol (ml) | Erythrocyte | Lymphocyte | Thrombocyte | Granulocyte |
| 1 | -- | 1,000 | -- | -- | -- | 293 | 2 | 5 | -- |
| 2 | -- | 999 | 0.97 | -- | 0.03 | 292 | 2 | 6 | -- |
| 3, 4, 5 | 100 | 999 | 0.92 | 0.056 | 0.024 | 293 | 3 | 3 | 1 |
| 6, 7, 8 | 30 | 999 | -- | 0.688 | 0.312 | 290 | 3 | 7 | -- |



APPENDIX C
TOXICOLOGY DATA SHEETS

TOXICOLOGY DATA SHEET
UVITEX OBTM

Classification:

Synthetic organic fluorescent whitening agent.

Animal Toxicology:

Acute:

Oral - rat

LD₅₀ 10,000 mg/kg

Primary skin irritation - rabbit

Non-irritant (Draize score 0/8)

Eye irritation - rabbit

Non-irritant (score 0/110)

Skin sensitization - guinea pig

Not a sensitizer (0.1% suspension in saline)

Photosensitization - rabbit

No evidence of photosensitization
(0.1% suspension in saline)

Subacute:

14-week feeding - rat

No evidence of toxicity was observed up to
10,000 ppm in the feed (approximately 5000 mg/
kg/day), the maximum concentration tested.

3-month oral - dog

No effect was observed at 2.5 mg/kg/day (in
gelatin capsules). At 250 and 2500 mg/kg/day
there were no effects other than frequent
loose yellowish stools.

Chronic:

1-year feeding - mouse (including 3-generation reproductive study)

At 1000 ppm (equivalent to 50 mg/kg/day) in the diet there were no observed differences from control animals in any parameters including tumor incidence. On ultraviolet illumination of tissue specimens, fluorescent deposits were seen in adipose tissue.

2-year feeding - rat

At 1000 ppm in the diet, there were no observed differences from control animals except slight liver enlargement in male rats, and an increased incidence of optical lens opacities of trefoil or Y-shaped configuration. Liver function tests, and liver histology, were not different from controls.

Human Toxicology:

Primary Skin Irritation and Sensitization:

No evidence of irritation or sensitization was observed in 102 subjects who were patched for 48 hours with 0.5 and 1% Uvitex OB in low-melting paraffin, and challenged with another patch 2 or 3 weeks later.

Symptoms of Poisoning:

No cases of poisoning with Uvitex OB have been reported. In animal tests, oral administration of large repeated doses caused diarrhea in dogs.

First Aid and Treatment:

For skin contact: wash with soap and water
For eye contact: flush with water for 15 minutes
For swallowing: since Uvitex OB is of low toxicity, ingestion of small amounts should require no treatment other than a saline laxative. In case of massive ingestion, if conscious, give water and induce vomiting or lavage stomach. Give supporting therapy.

Handling Recommendations:

In accord with good industrial practice, handle with due care and avoid unnecessary personal contact.

TOXICOLOGY DATA SHEET

NOPOL

(NORDA, INC.)

Synonyms: 6.6-Dimethylbicyclo-(3.1.1)-2-heptene-2-ethanol.

Description and physical properties: A colorless liquid.

Preparation: By condensation of beta-pinene with formaldehyde under pressure (Arctander, 1969).

Uses: In public use since the 1940s. Use in fragrances in the USA amounts to approximately 10,000 lb/yr.

Concentration in final product (%):

| | <u>Soap</u> | <u>Detergent</u> | <u>Creams, lotions</u> | <u>Perfume</u> |
|---------|-------------|------------------|------------------------|----------------|
| Usual | 0.03 | 0.003 | 0.015 | 0.3 |
| Maximum | 0.25 | 0.025 | 0.08 | 1.2 |

Analytical data: Infra-red curve, RIFM No. 76-374.

Status

Nopol is not included in the listings of the FDA, FEMA (1965), the Council of Europe (1974), or by the Food Chemicals Codex (1972). CAS Registry Number 128-50-7.

Biological Data

Acute toxicity. The acute oral LD₅₀ value in rats was reported as 0.89(0.61-1.29g/kg) and the acute dermal LD₅₀ value in rabbits exceeded 5g/kg (Moreno, 1977). The im LD₅₀ for nopol in mice was 0.5 g/kg (Northover & Verghese, 1962).

Irritation. Nopol applied full strength to intact or

abraded rabbit skin for 24 hours under occlusion was moderately irritating (Moreno, 1977).

Tested at 8% in petrolatum it produced no irritation after a 48 hour closed patch test on human subjects (Epstein, 1976).

Sensitization. A maximization test (Kligman, 1966; Kligman & Epstein, 1975) was carried out on 29 volunteers. The material (RIFM # 76-374) was tested at a concentration of 8% in petrolatum and produced no sensitization reactions (Epstein, 1976).

Pharmacology. In the anesthetized dog, 23 mg/kv iv of nopol produced a 25% fall in blood pressure. Hypotensive effects were also noted in the decerebrated and despinalized dog (Northover & Verghese, 1962).

Isolated tissue. Nopol (50 mg), when added to the perfusate of the isolated hind leg of the anesthetized dog or isolated rabbit ear, produced vasodilation (Northover & Verghese, 1962).

References

- Arctander, S. (1969). Perfume and Flavor Chemicals (Aroma Chemicals). Vol. II, no 2383. S. Arctander, Montclair, New Jersey.
- CIVO-TNO (1977). Volatile compounds in Food. 4th edition. Centraal Instituut Voor Voedingsonderzoek ENO. Edited by S. Van Straten. Zeist, Netherlands.
- Council of Europe (1974). Natural Flavouring Substances, Their Sources, and Added Artificial Flavouring Substances, Partial Agreement in the Social and Public Health Field. Strasbourg.
- Epstein, W.L. (1976). Report to RIFM, 20 December.
- Flavoring Extract Manufacturers' Association (1965). Survey of flavoring ingredient usage levels. Fd Technol., Champaign 19(2), part 2, 155.
- Food Chemicals Codex (1972). 2nd ed. Prepared by the Committee on Specifications, Food Chemicals Codex, of the Committee on Food Protection. National Academy of Sciences-National Research Council Publ. 1406, Washington, D.C.
- Kligman, A.M. (1966). The identification of contact allergens by human assay. III. The maximization test. A procedure for screening and rating contact sensitizers.

J. invest. Derm. 47,393.

Kligman, A.M. & Epstein, W. (1975). Updating the maximization test for identifying contact allergens.

Contact Dermatitis. 1, 231.

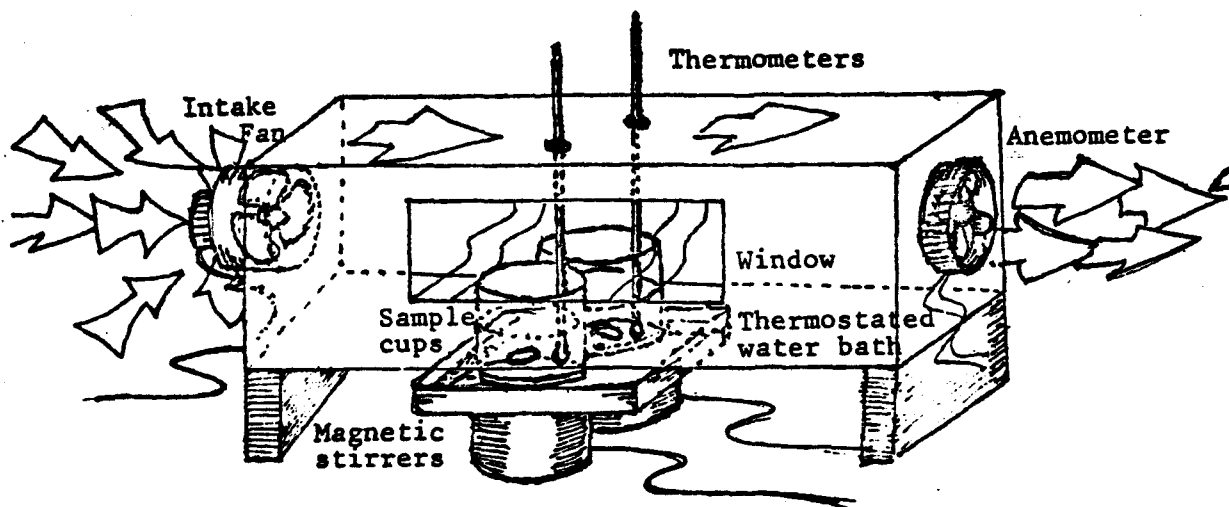
Moreno, O.M. (1977). Report to RIFM, 2 February.

Northover, B.J. & Verghese, J. (1962). The pharmacology of certain terpene alcohols & oxides. J. scient. ind. Res. 21C, 342.

APPENDIX D

VOLATILITY AND FLASH POINT STUDIES

Static tests were run, on both gelled and ungelled liquids in closed manometric systems; the results of these tests strongly bear out that there is no significant effect on the vapor pressure exerted by the system. Dynamic tests, to be described, showed very significant advantages for gelled vs. ungelled systems. Using the apparatus shown below, reductions in excess of 50% of the rates of evaporation for compounds such as hexane, ether, and similar volatile compounds with limited solubility in water, have been observed for the gelled liquids.



DYNAMIC VOLATILITY APPARATUS

In practice, the two cups seen through the window in the wind tunnel are half filled with water, and then layered, in one cup, with ungelled liquid. The other cup is layered with a 10% solution of Amine D solution in the liquid, the entire solution then being gelled with carbon dioxide in the form of a few pieces of Dry Ice. The cups are thermostated in a water bath to a temperature of 25° C., and winds of various velocity (usually around six knots, wind velocity being measured by the anemometer) are passed over the cups using the fan indicated above. Weights of the cups are taken on a periodic basis. In

the case of the gelled liquids, a crust soon forms on the evaporation. It is strongly indicated that reductions in fire hazards for flammable liquids, and in toxicities of poisonous liquids, would be desirable consequences of this effect.

In an effort to quantify any effects in reduction of fire hazards, open flash points were determined; the results of these tests are shown in the following table.

(The same wind tunnel as was used in the previously described volatility experiment was utilized to direct a five-knot wind onto the open cup of a flash point apparatus, in keeping with the previously described volatility experiment.)

| Compound | Flash Point, °C UNGELLED | | Flash Point, °C GELLED | | Literature Value* |
|----------------|-----------------------------|----------|---------------------------|----------|----------------------|
| | Trial I | Trial II | Trial I | Trial II | |
| Cyclooctane | 52.5 | 53.0 | 63.5 | 62.0 | |
| 1-Dodecene | 92.5 | 91.5 | 93.0** | 94.0** | |
| Ethylbenzene | 36.5 | 36.0 | 49.5 | 54.0 | 23.8 |
| Ethyl Butyrate | 39.5 | 38.0 | 41.5 | 41.5 | 29.4 |

* Lange's Handbook of Chemistry, 9th ed., edited by W. A. Lange, Handbook Publishers, Inc., Sandusky, Ohio, 1956; pp. 32-49.

Literature values are significantly lower than ungelled values in this experiment, inasmuch as in this experiment a five-knot wind current is being utilized.

** The 1-dodecene gel began to melt at about this temperature.

As can be seen from the above data, significant flash point elevations were achieved, particularly for the hydrocarbons which did not melt, upon gelation.

APPENDIX E

SUBMISSIONS OF PRODUCT LISTINGS FOR INCLUSION IN SURVEY OF EQUIPMENT FOR OIL AND FLOATING HAZARDOUS MATERIAL SPILL COUNTERMEASURES

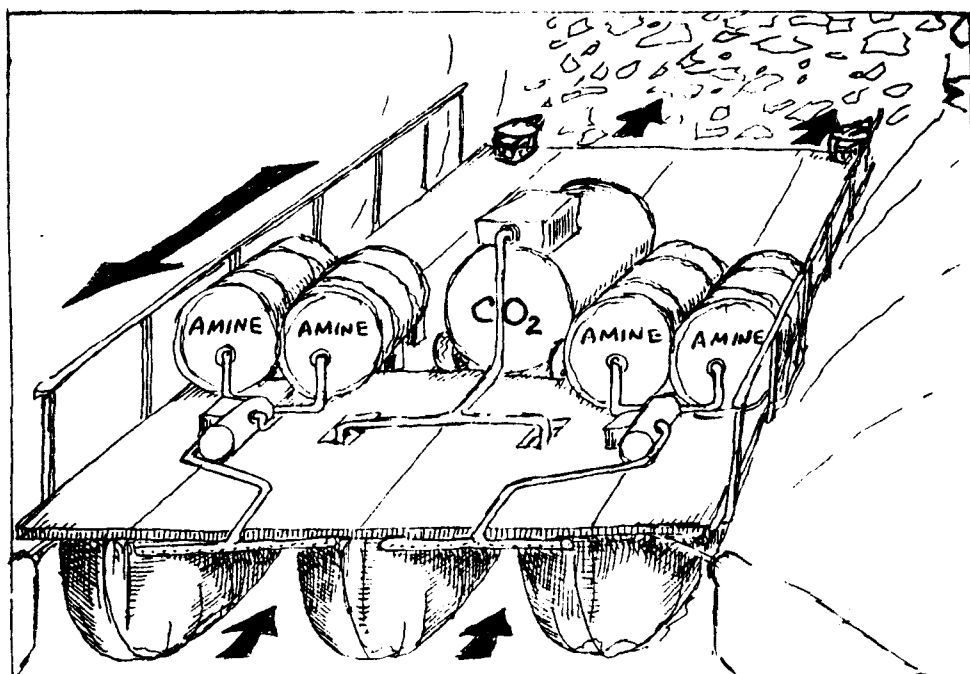
Product Listing: AMINE CARBAMATE GELLING AGENTS

- 1.3 Containment on or in water
 - Fluid barriers
- 1.4 Air containment or vapour suppressor
 - Physical
- 2.2 Recovery from water
 - Floating substances
 - sorbant surface devices
- 3.2 Systems for liquids
 - Other (immobilization of oil and floating hazardous liquids by gelatin, thereby reducing spreading rate over water surfaces)
 - Other (use of nets in recovery of gelled oil and floating hazardous liquids)
- 4.2 Systems for liquids or solids
 - Other (use of plastic bags, cardboard boxes, etc. for storage of recovered gelled oil and hazardous liquids)
 - Other (reduction of shipboard free surface effects by gelation of stored recovered oil and hazardous liquids)
- 7.3 Treating agents
 - Physical converting agents
 - gelling agents
 - other (increased visibility of oil and hazardous liquids by conversion to opaque white floating chunks of gel)

Brief Description

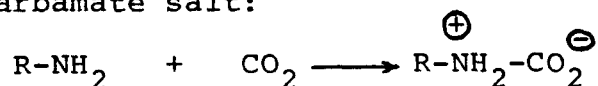
AMINE CARBAMATE GELLING AGENTS

This system is intended to facilitate recovery and control of oil and hazardous liquids on water surfaces. A trimaran is equipped with forward mounted sprayers fed by an amine solution pumped from deck tanks; a liquid CO₂ transit tank and sparging system aft of the sprayers; and nets towed behind the craft to recover the gelled liquid. The gelling reaction has been fully tested; the trimaran is still under development, one prototype having been built and successfully tested.



Operating Principle:

The process depends on the reaction of CO₂ and an amine, to form a carbamate salt:



The spill is directed into the path of amine sprayers by sweeps or booms at the front of the trimaran, and thence between

the pontoon hulls. Liquid CO₂ is directed into this mixture, and the resulting carbamate solidifies the entire liquid system into white floating chunks of gelled material.

The solidified oil or hazardous liquid is considerably less mobile and will not readily spread back over the track previously cleaned by skimmer craft, as would be the case for ungelled material. Being white and opaque it is much easier to see; due to its solid consistency it can be recovered by nets towed aft of the trimaran, and then stored in bags or boxes which would otherwise be unsuitable for liquid recovered material. The solid nature of the gelled liquid also prevents spread of ungelled liquid areas contiguous to gelled areas. Free surface ("sloshing") effects which tend to destabilize vessels carrying recovered liquid pollutants are obviated by conversion to the solid gelled state. Gelled liquids have greatly reduced evaporation rates and higher flash points, with decreased toxicity and fire hazards. Should gelled pollutants wash up on a beach, the solid form will not penetrate the sand or soil as would ungelled liquids. The pollutant can be recovered by subjecting the gelled material to pressure filtration, with recovery also of the carbamate gelling agent which can then be converted to the starting amine by thermal decarboxylation.

Physical Specification:

| | |
|---|--|
| Amine Solution (to be applied in about 15 % concentration): | A three component solution is used: 70% Amine D TM (dehydroabietylamine, manufactured by Hercules); 15% ethanol; and 15% Nopol (6,6-dimethyl-2-norpinene). |
| Vessel: | Modular trimaran, capable of assembly in less than two hours; when disassembled can be stored and transported in a 2.5x3.7x1.8 meter (8'x12'x6') truck trailer with all required equipment and supplies. Pontoons are perforated polycarbonate |

shells clamped around inflatable rubber bladders. Deck consists of marine plywood panels laid over aluminum bracing. Overall assembled length (without extended sweeps), 7.3 meters (24 feet); width, 3.7 meters (12 feet). Draft with full loading, 0.4 meter (17"); freeboard 0.5 meter (23").

Ancillary
Equipment:

Eight 55-gallon (206 liter) drums of Amine D solution; CO₂ transit tank (320 kg., or 700 lb capacity) with hose and sparging system; metering pumps (two) for Amine D solution; Amine D sprayers (two); 220-volt electrical generator (gasoline powered) and GFI (Ground Fault Interrupter) equipment; forward-mounted sweeps for increased width of intake area; two 25-HP marine engines. Life rafts, life jackets, tool and damage control locker. Additional drums of Amine D solution, as may be required, would be stored and transported separately. For situations involving recovery and control of more than 5,000 gallons (18,750 liters) of pollutant liquid spills on water surfaces, a back-up CO₂ transit tank is recommended also. Liquid CO₂ for filling of transit tank would be obtained from CO₂ facility en route to spill site.

Cost:

Trimaran craft and all equipment: \$70K (U.S.).

Supplies: For each 200 kg. drum of Amine D solution, capable of

application to 1350 liters
(360) gallons of pollutants
\$900 (U.S.).

Liquid CO₂: Refill of transit tank: approx. \$300.

Operating
Specifications:

Vessel designed for operation in inland waters or in situations with less than 0.5 meter (1 1/2-foot harbor chop situations.

Craft will support a load of five metric tons of equipment and supplies, at a fully laden speed of about 3 1/2 kts (6.5 km/hr), and can cover an area of about 0.4 hectare (one acre) in a track five meters wide by 0.8 km (16 1/2 feet by 0.5 mile), with 8200 liters (2200 gallons of pollutant spill, in less than 10 minutes. Recovery nets towed by auxiliary craft stationed behind the trimaran could be deployed to recover the gelled pollutant.

Assembly and loading of the trimaran can be accomplished at a boat landing, or by lowering raft and component equipment from overhead bridges to water surface by means of a one-ton crane.

Usage:

Prototype successfully tested at US Naval Submarine Base, New London, CT on 17 December 1979, and successfully used there later on an actual spill.

- No quantitative results.

" . . . successful gellation of an actual spill on 31 December 1979 at the Naval Submarine Base New London, Groton, CT.

. . . The gelation of oil by amine carbamates would be feasible and economical under certain conditions. (Report of Commanding Officer, Naval Submarine Support Facility, New London to Commander, Naval Facilities Command, dated 25 Feb 1980.)

Availability
and Commercial
Information:

Patents: U.S. 3,684,733 and 3,880,569.

Publication: "Amine Carbamate Gelling Agents for Facilitating Oil Spill Recovery and Control", Marine Technology, October 1980, pp. 146-149.

Manufacturer: University of Lowell
Lowell, MA 01854
Phone: (617) 452-5000,
x2509
Contact: W. Bannister

Product Listing: FLUORESCENT AGENTS FOR NIGHT-TIME OPERATIONS

7.3 Treating agents

- Combination or other (fluorescent agents for night-time oil or hazardous liquid spill recovery and control operations)

Brief Description:

FLUORESCENT AGENTS FOR NIGHT-TIME OPERATIONS

This system is intended to facilitate recovery and control of liquid spills on water surfaces. Commercially available, non-toxic, cheap and highly efficient fluorescing agents with both oil and water solubility are applied in very low concentrations to liquid spills with excellent results. In open water the agent is dissipated into the water column, but is preferentially retained in pollutant patches on the water surface. At night UV light is beamed over the spill area with illumination by resulting fluorescence occurring only from patch areas. Excellent contrast between pollutant patches and open water areas is thereby obtained, such discernibility enabling night-time spill recovery and control operations.

Operating Principle:

A solution of the fluorescer is sprayed from aircraft on the spill area to a concentration of 10 ppm (0.001%) in the pollutant spill. That portion landing on spill patches is retained; spray landing on open water is dissipated into the water. At night a skimmer with longwave (366 nm) UV lights is deployed. Ordinary visible searchlights are operated intermittently to illuminate floating debris in the path of the craft. During periods of searchlight darkness UV effected fluorescence from the pollutant patches will provide adequate perception of perimeters of these patches.

Physical Specification:

Fluorescer
Solution: UVITEX OBTM stilbene fluorescer manufactured by Ciba-Geigy, Inc, in a glycol ether solvent (concentration of solution about 1%).

Ancillary
Equipment: Conventional crop-spraying equipment as used in aerial spraying operations. UV lights (under development). (In test operations racks of 1.8 meter, or six foot 85-Watt UV fluorescent lamps have been used successfully.) Suitable helicopter or fixed-wing aircraft for agent delivery.

Cost: For application over 2.5 hectare (25,000 m², or ten US acres) it is anticipated that the fluorescer agent and solvent would cost about \$300 (US).

Operating
Specifications: (See discussion under Operating Principle.)

Usage: Small (10 m²) areas tested at OHMSETT (August 1979).
- No quantitative results.

Availability
and Commercial
Information: Applications for patent coverage in progress.

Publication: Marine Technology,
October 1980, pp. 146-149

Manufacturer: University of Lowell
Lowell, MA 01854
Phone: (617) 452-5000,
x2509
Contact: W. Bannister

SUMMARY TABLE A:

Equipment, System or Material Type

| | Use Documented | Tested | Development Underway |
|---|----------------|--------|----------------------|
| 1. Containment | | | |
| 1.3 Containment on or in water | | | |
| - Fluid barriers | X | X | X |
| 1.4 Air containment or vapour suppressor | | | |
| - Physical | X | X | X |
| 2. Mechanical Recovery | | | |
| 2.2 Recovery from water | | | |
| - sorbant surface devices | X | X | X |
| 3. Transfer Systems | | | |
| 3.2 Systems for liquids | | | |
| - Other (immobilization of pollutants by gelation, thereby reducing spreading rate over water) | X | X | X |
| - Other (use of nets in recovery of gelled pollutant) | X | X | X |
| 4. Temporary Storage | | | |
| 4.2 Systems for liquids or solids | | | |
| - Other (use of plastic bags, cardboard boxes, <u>etc.</u> for storage of recovered gelled pollutant) | X | X | X |
| - Other (reduction of shipboard free surface effects by gelation of stored recovered pollutant) | X | X | X |
| 7. Treatment | | | |
| 7.3 Treating agents | | | |
| - Physical converting agents | | | |
| - gelling agents | X | X | X |
| - other (increased visibility of pollutants by conversion to opaque white floating chunks of gel) | X | X | X |

SUMMARY TABLE A:

CATEGORIZATION BY BEHAVIOUR AND PROPERTY OF MATERIALS ON THE EEB PRIORITY LIST OF SUBSTANCES

General applicability:

Liquids: High, medium, or
low flammability

Specific Gravity
less than 1.00

Little reaction or
low miscibility
with water

1.3 Containment on or in water

- Fluid barriers

1.4 Air containment or vapour suppressor

- Physical

2.2 Recovery from water

- sorbant surface devices

3.2 Systems for liquids

- Other
- Other

4.2 Systems for liquids or solids

- Other
- Other

7.3 Treating agents

- Physical converting agents
 - gelling agents
 - other

LEGEND:

T = Tested only

P = Possible application to
substance

Group A

Group B

| | | | |
|---|---------------------|---|---------------------|
| T | Benzene | T | Carbinol |
| T | Ethyl Benzene | P | Isobutyl Ketone |
| T | Styrene (monomer) | P | Methyl Methacrylate |
| T | Toluene | T | n-Hexane |
| T | Xylenes | P | Tall Oil |
| T | 2-Ethylhexanol | T | Turpentine |
| P | Butyl Aldehydes | | |
| T | Cumene | | |
| T | Cyclohexane | | |
| P | Ethyl chloride | | |
| P | Methyl Isobutyl | | |
| T | Methyl Isobutyl | | |
| P | Methyl Methacrylate | | |

NOTE: All items indicated to the left
apply as indicated above.

Virtually all compounds listed
in Group A and Group B Tables,
and not included in above
listing due to solid state or
density greater than 1.0
characteristics, are gelled by
this system in situations
wherein these are dissolved in
suitable solvents. For
example, solutions of dichlo-
robenzene in hexane are gelled
by amine carbamates.

SUMMARY TABLE A:

Equipment, System or Material Type

7. Treatment

7.3 Treating agents

- Combination or other (fluorescent agents for night-time hazardous liquid spill recovery and control operations

Tested
Development
Underway

X X

SUMMARY TABLE B:

CATEGORIZATION BY BEHAVIOUR
AND PROPERTY OF MATERIALS ON THE
EEB PRIORITY LIST OF SUBSTANCES

Group A

Group B

General applicability:

Liquids: High, medium or
low flammability

Specific Gravity
less than 1.00

Little reaction or
low miscibility
with water

7.3 Treating agents

- Combination or other

| | |
|-------------------|--------------------------|
| Benzene | Butyl Aldehydes |
| Ethyl Benzene | Cumene |
| Styrene (monomer) | Cyclohexane |
| Toluene | Ethyl Chloride |
| Xylenes | Methyl Isobutyl Carbinol |
| 2-Ethylhexanol | Methyl Isobutyl Ketone |
| | Methyl Methacrylate |
| | n-Hexane |
| | Tall Oil |
| | Turpentine |

T T T T T T P T T P P T P T P T

LEGEND:

T = Tested only

P = Possible application
to substance

NOTE: Virtually all compounds listed in Group A and Group B Tables, and not included in above listing due to solid state or density greater than 1.0 characteristics, are applicable to this fluorescence system, in those cases wherein these are dissolved in suitable solvents. Thus, a solution of dichlorobenzene in hexane will fluoresce under UV after being sprayed with this fluorescer solution.

APPENDIX F

NEAR-SURFACE WATER COLUMN PROFILING BY ACOUSTIC SENSING AS A COMPLEMENTARY MEANS TO DEFINE EXTENTS OF LOW-VISIBILITY OIL AND HAZARDOUS CHEMICAL SPILLS

Background

(The following remarks, regarding acoustic sensing as a means of studying oceanic pollution problems, are abstracted from a paper delivered by J. R. Proni of NOAA, at the 1980 Ocean Acoustic Remote Sensing (OARS) Workshop.

"The use of acoustics in studying oceanic pollution problems has risen substantially in the last five years. Since that time numerous uses of acoustics have been made in studying dumped materials; these materials include sewage sludge, dredge material, petrochemical wastes, industrial wastes, pharmaceutical wastes, sub-surface oil (from the IXTOC-1 oil spill) and, recently, drilling muds."

"One of the most important characteristics of a given volume of oceanic water is the rate at which elution of a given dump material occurs in that water. There are various factors which influence the dilution rate; these include water column stratification, currents and dispersion (turbulent) characteristics. Accurate dilution rates are extremely difficult to obtain. However, estimates may be made of horizontal dispersion coefficients, K , which are fundamental in dilution rate predictions."

(Additional remarks by M. H. Orr of the Woods Hole Oceanographic Institution, at the OARS Workshop, are abstracted below.)

"Remote acoustic sensing of atmospheric fluid processes has developed into an active research discipline. There are a large number of applied and basic atmospheric research groups using the acoustic technique in both the monostatic and bistatic modes of operation. These groups study both fluid and biological processes. In contrast, the number of researchers actively using or evaluating

the use of high frequency remove acoustic sensing to study oceanic fluid processes is quite limited. Although a few people actively pursued the potential, the oceanographic community has not adopted the technique as a tool. This lack of interest may be due to the discipline's past preoccupation with trying to understand oceanic circulation on a mesoscale and also the uncertainty in interpreting the acoustic records without complementary in situ data."

"The acoustic system developed at the Woods Hole Oceanographic Institution has been used to study:

- (1) sewage sludge and particulate distribution in Boston Harbor,
- (2) fluid processes such as internal waves, shear instabilities, air-sea interactions, shelf-slope frontal zone, interleaving water masses, and hydraulic jumps across wills, and
- (3) the seasonal dispersion properties of particulates released or formed during industrial chemical and sewage sludge disposal at Deep Water Dumpsite 106 (DWD 106). The research has been conducted in Boston Harbor, Massachusetts Bay, on the eastern continental shelf, in Puget Sound, and in the open ocean."

"Theoretical considerations indicate that the dominant mechanisms anticipated for the oceanic environment are:

- (1) backscattering from laminae or isotropic temperature fluctuations which are developed during turbulent mixing events,
- (2) backscattering from temperature steps or gradients, and
- (3) backscattering from particulate distributions (either animate or inanimate) associated with varying water masses. For example, nearly neutrally buoyant particles, when falling through the water column, could have a tendency to collect at density discontinuities associated with temperature steps in the water column. Consequently,

an acoustic backscattering system would be able to map the location of the density step and associated thermal step and the step's response to internal wave activity and mixing processes."

Conclusion

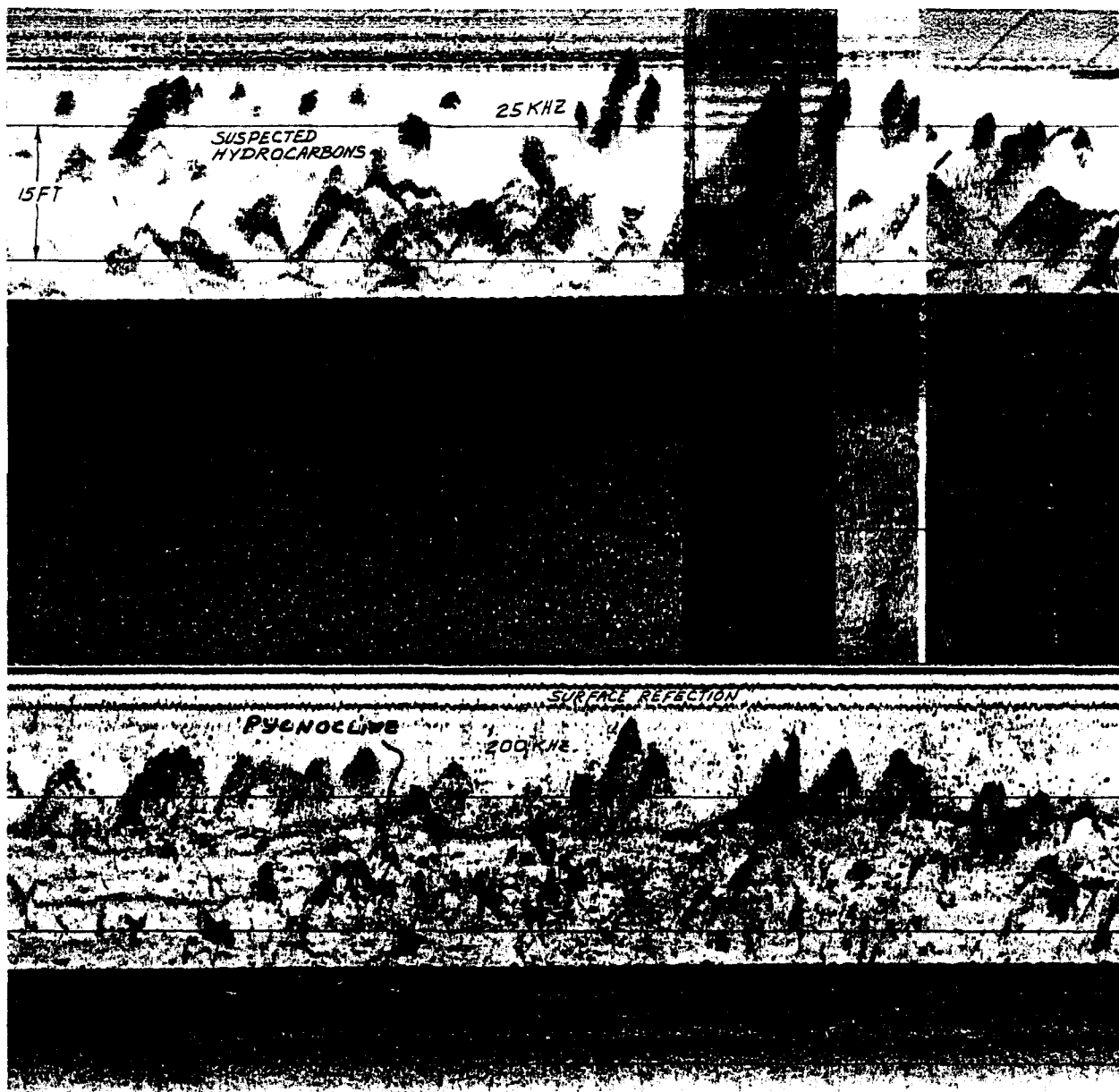
"A general overview of the results calls attention to the potential of using high frequency acoustic back-scattering systems in the study of:

- I. A variety of fluid processes:
 - A. Internal waves
 - B. fronts
 - C. mixing
 - D. interleaving water masses
- II. Particulate distributions:
 - A. natural in estuary, shelf, and open ocean environment
 - B. manmade in estuary, shelf, and open ocean environment
 1. dredge spoils
 2. industrial chemical wastes
 3. sewage sludge
- III. Biology
 - A. fish stock assessment
 - B. zooplankton biomass
 - C. predator-prey interactions
 - D. Biological avoidance of oceanographic instrumentation
 - E. Biological response to fluid processes."

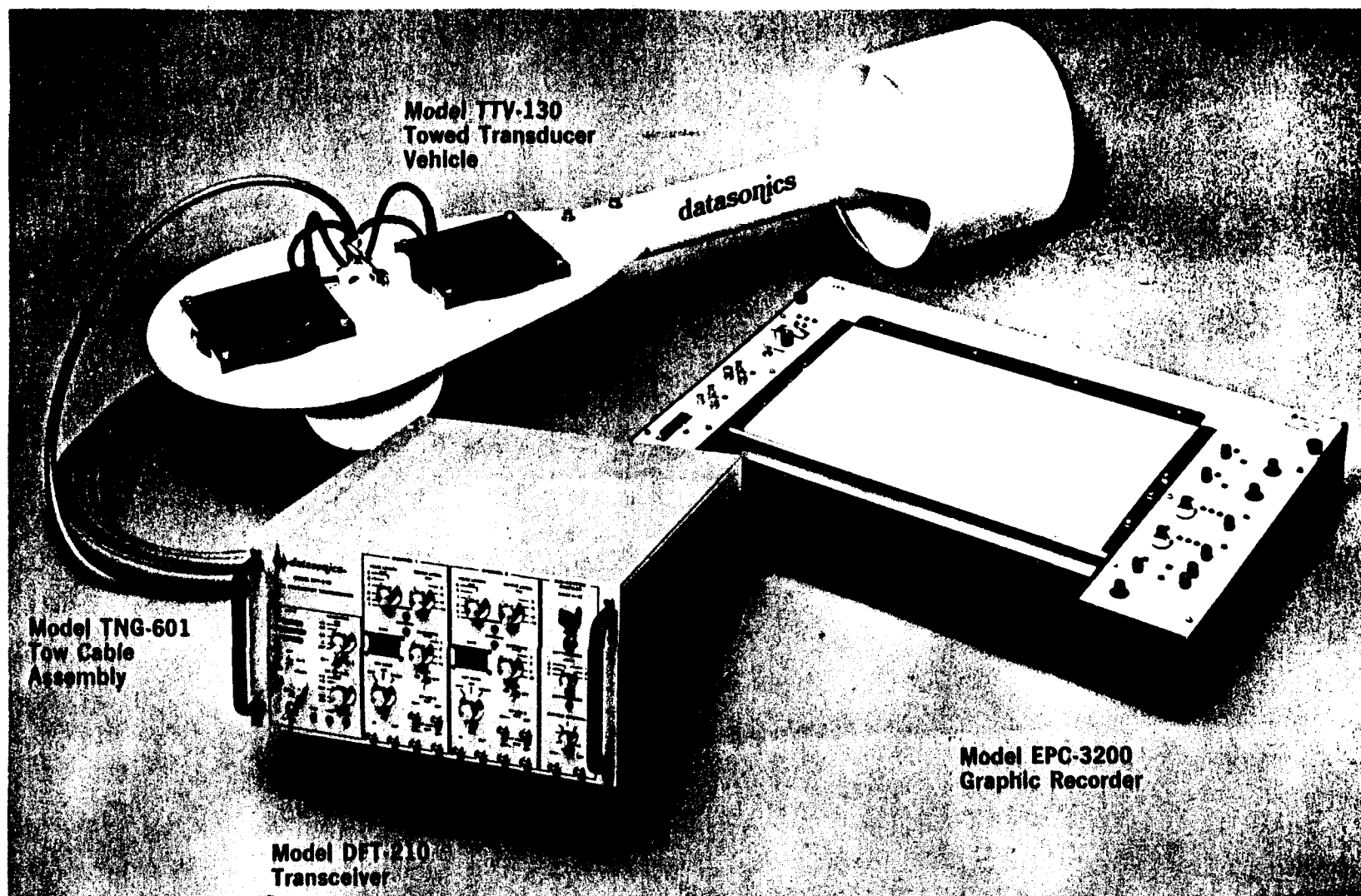
From the foregoing statements it would appear that the use of a device which can be carried at the surface of a water column and can give information in real time about the

density of particles at every depth along the water column has appeal in research at sea. Such a device, acoustic echo sounding and sensing equipment described above does exist and its practicability has been demonstrated. Whether the resolution of particle sizes is shape dependent (as it is in the case of light scatter as a function of wavelength) remains to be determined. It is not clear at this time either as to the contribution to the changes in composition of the echoes from column that will be changed by other parameters which can be measured throughout the length of the column. Just as in the case of light, sound will be scattered in various ways, depending upon the size and shape of particles, and the refractive properties of the containing medium. However, the prediction of the existence of particles having particular characteristics may be more difficult than is the case with light. No doubt, some of the parameters which are monitored presently as indices of the condition of state and the quality of water will to some extent alter the propagation of sound wave fronts. We wish to record several of these indices at sites which are being simultaneously probed with a surface carried echo sounder operating from 3 to 300 kHz, using the Datasonics Model DFS-2100 Environmental Echo Sounding System; see accompanying information.

High frequency acoustic backscattering techniques have the potential for becoming a valuable tool in oceanographic research and monitoring exercises. These will be able to work in both a complementary and a stand-alone format.



SCIENTIFIC ECHO SOUNDING FOR STUDY OF FATE
OF SUSPECTED HYDROCARBON POLLUTANTS



MODEL DFS-2100 DUAL FREQUENCY SCIENTIFIC ECHO SOUNDER

CAPABILITIES

Location, tracking and mapping concentrations of biological activity.

With a sample taken to ground truth the acoustic record, a fast, accurate survey can be performed.

The calibrated acoustic system allows calculation of target strength of individual scatterers, or reverberation level of scattering layers.

Water column processes including internal waves, interleaving water masses, shear discontinuities etc. can be detected and mapped as part of circulation modeling projects as well as other types of oceanographic research programs.

Tracking dispersions of drilling effluents pumped from offshore drill rigs.

Location and tracking position of plumes resulting from sewage sludge, chemical waste and other potentially toxic material dumped in the ocean.

Survey of dredge spoil dispersion.

Location and tracking position of hydrocarbons in the water column resulting from spills or natural seepage.

Study of sewage treatment plant outfall effluent dispersion.

Analysis of in water pollutant location, origin, and ultimate destination.

Port and harbor environmental studies associated with construction projects.

Component Description Model DFT-210 Transceiver:

The high power, two channel calibrated transceiver generates two independent transmit signals over a frequency range between 3kHz and 300 kHz. Dual channel low noise, high gain receivers provide calibrated outputs which incorporate accurately controlled time varying gain to compensate for spreading and attenuation losses. Wide system dynamic range allows processing of large and small scatterers throughout the water column.

Model TTV-130 Towed Transducer Vehicle:

A light weight tow fish with two transducers installed for

operation at customer specified frequencies between 3 kHz and 300 kHz. Constructed from corrosion resistant stainless steel and fiberglass, the vehicle can be easily deployed and recovered by a single person.

Model EPC-3200 Graphic Recorder:

A 19 inch dry paper two channel recorder for simultaneous display of data at the two selected system operating frequencies. The recorder has an internal data memory which allows selective data expansion and display of water column or sub-bottom sediment data in the best possible format. Memory capability allows data display free of interference problems associated with second bottom multiple echos.

Tow Cable Assembly:

Tow cables are available in different lengths with either external armoring or a Kevlar braid with urethane jacket to provide the required breaking strength. A stainless kelly grip or molded epoxy retention provides a termination at the tow fish end of the cable. High quality Brantner Sea-Con connectors are utilized. Internal dedicated coaxial conductors provide best isolation between channels with lowest possible noise insertion.

SPECIFICATION FEATURES

Wide Range of Operating Frequencies:

Simultaneous dual frequency operation over frequency range from 3 kHz to 300 kHz. Channel 1 frequency adjustable in 10 Hz steps, Channel 2 in 250 Hz steps.

High Transmitter Output:

4 KW power output each channel, adjustable in 3db steps, open and short circuit protected.

Selectable Pulse Width and Repetition Rate:

Internal or External control of repetition rate up to 8 pps. Selectable pulse widths from 100 μ sec to 2 msec.

Superheterodyne Receiver Utilizes Precise Mechanical Bandpass Filters:

Superheterodyne design allows calibrated control of signal processing over wide frequency range. Bandwidth selection 1, 2, 5 or 10 kHz.

Low Noise High Gain Receiver Design:

Use of a very low noise preamplifier and high overall system gain capability allows detection of small size particle scatters and low concentrations of particulate matter. GAIN control is provided in calibrated 3 db steps.

Accurate Time Varying Gain (TVG) Control and Wide Dynamic Range:

Allows processing of both large scatterers at close range and small, more distant scatterers. With greater than 80 db range and a selectable range reference between 1 meter and 100 meters, operation is possible in both shallow and deep waters areas.

Accurate Transmission Loss Compensation:

The TVG control provides spreading loss compensation at both 20 Log R and 40 Log R rates with adjustable $2 \propto R$ attenuation loss compensation.

Multiple Receiver Outputs:

Calibration:

A calibrated self test signal is available for providing a field calibration check for proper system operation.

Sub-Bottom Profiling Feature:

Adjustable calibrated sub-bottom TVG with automatic bottom tracking for optimum high resolution profiling of sediment structure. Calibrated output allows calculation of relative reflection strength of successive sub-bottom layers.

Transducer Selection:

Several transducers are available over the frequency range; including units operating at 3.5 kHz, 7.0kHz, 12kHz, 25kHz, 37 kHz, 50 kHz, 85kHz, 120 kHz, 200 kHz and 300 kHz. Beamwidths vary with transducer physical dimensions and can be tailored as required. All units are constructed of piezo-electric ceramic arrays installed in a pressure compensated oil filled housing.

APPENDIX G

REPORT OF OIL SPILL CONTROL AND RECOVERY FIELD TESTS AT
US NAVAL SUBMARINE BASE, NEW LONDON, CONN.

NSSF:630:das:Dicta/A
6240
Ser 000244
25 FEB 1980

From: Commanding Officer, Naval Submarine Support Facility
New London,

To: Commander, Naval Facilities Engineering Command

Subj: Gelation of oil by amine carbamates; test and
evaluation of

Ref: (a) COMNAVFACECOM 1tr 1123C/PCH of 3 Jul 79
(b) CO, NAVSUBSUPPFACKLON 1tr Ser 1239 of 30
Jul 79
(c) U.S. Environmental Protection Agency Region I
ltr of 31 Oct 79
(d) State of Connecticut Department of Environ-
mental Protection 1tr of 6 Nov 79

Encl: (1) Photographs taken 8 Nov 79 of first attempts
at gelation (7)
(2) Photograph taken 21 Dec 79 and sketch showing
assembly of workable components
(3) Photographs taken 31 Dec 79 showing utilization
in an actual spill situation (4)

1. Reference (a) requested that the Naval Submarine Support Facility New London perform a limited oil spill clean-up test and evaluation of an oil gelling agent; which depends on the action of carbon dioxide on amine which forms a sludge like material when combined with oil and forms gelation of the oil it contacts. Once gelled the solution is to be picked up by mechanical means such as shovel, nets or large scopes. This method has been developed by the University of Lowell for the Naval Facilities Engineering Command. Reference (b) requested authorization for subject test and evaluation to be conducted by the Naval Submarine Support Facility New London. References (c) and (d) approved

the use of the gelling agent in the clean-up of a spill of opportunity.

2. An initial test and demonstration by the University of Lowell team, with assistance from the Naval Submarine Support

Facilities New London Pollution Control personnel on 8 November 1979, was unsuccessful due to inability to regulate air pressure within the amine carbamate distribution system. Enclosure (1) contains photographs of the equipment used. Enclosure (2) provides a photograph and sketch of a simplified system recommended by the Naval Submarine Support Facility New London personnel. A successful test using the modified equipment was conducted on 17 December 1979. Enclosure (3) contains photographs of the successful gel-lation of an actual spill on 31 December 1979 at the Naval Submarine Base New London, Groton, Connecticut.

3. The gellation of oil by amine carbamates would be feasible and economical under certain conditions. The following are examples:

a. Inside of drydocks where staging and blocks prevent the maneuvering of present mechanized equipment (DIF 3001).

b. The boundaries of marsh areas where the gellation of oil would reduce or prevent further mitigation of oil due to its adherence to boundary vegetation.

c. For blocking the flow of oil through breakwaters, canal banks, or quays etc. by accumulation of the gelled product in the passageways.

T.C. Maloney

Copy to: (w/o enclosures)
University of Lowell, Lowell MA
State of Connecticut Department of Environmental Protection,
Hartford, CT
Seas International, LTD, Needham, MA
COMSUBGRU TWO
COMSUBRON TWO

APPENDIX H

FLUORESCENT AGENTS FOR NIGHT-TIME OPERATIONS: RESULTS OF TESTS ABOARD EPA OSV ANTELOPE, 14 SEPTEMBER 1981

Time: Approximately 9:30 - 10:15 PM

Location: Approximately five miles ENE of eastern terminus of Cape Cod Canal, in Cape Cod Bay, Massachusetts

Ship Speed: Approximately four knots

Weather Conditions:

- Temperature: Approximately 60°F (15°C)
- Wind: Approximately 5 knots, varying gusts during squalls
- Waves: Calm
- Visibility: Full moon, obscured by occasional cloud cover with intermittent rain squalls. Overall excellent visibility.

Oil Spill: 30 gallons of fish oil obtained from Marine Products Company, Boston, Massachusetts, with characteristics as noted below. (Comparative data are also provided for cyclohexane as a standard, and #2 Fuel Oil as a typical material frequently encountered in oil spills in this area.)

| | Fish Oil (as received) | #2 Fuel Oil (as received) | Cyclohexane |
|-------------------------------|---------------------------|------------------------------|-------------|
| Density (g/ml) | 0.926 | 0.74 | |
| Surface Tension (dynes/cm) | 32.0 | 27.2 | 25.3 |

Fluorescer: UVITEX OBTM, manufactured by CIBA-GEIGY Corporation, Ardsley, NY. Weight used: 8.0 g (providing approximately 60 ppm concentration in fish oil). The

fluorescer was mixed with the fish oil in a 35-gallon drum prior to delivery onto water surface.

UV Lamps: Two 400-Watt Sylvania mercury vapor spotlights with phosphor removed to provide UV illumination, with about 5% of wattage in the 366 ± 5 nm fluorescence range of the UVITEX OB agent anticipated. One 565-Watt Hanovia Super-S Alpine sun lamp, manufactured in 1948; broad range spectrum with about 2% of wattage available in the 366 ± 5 nm fluorescence range. One 100-Watt mercury vapor spotlight with about 5% of wattage available in the 366 ± 5 nm fluorescence range.

Additional Equipment: Datasonics, Inc. Model DFS-210 Dual Frequency acoustic sensing device, tested by Datasonics on this occasion simultaneously with the fluorescence system. (Although there is no relationship between the fluorescence and acoustic systems, these were demonstrated to be synergistic, as will be described in ensuing discussion.)

DISCUSSION OF TEST

The fluorescer was mixed with the fish oil by use of wooden paddle stirring of the mixture in a 35-gallon drum. Prior to the test, also, two UV-sensitive fluorescent markers, in the form of 24' x 3' plastic "bubble-cap" sheets, one painted with fluorescent red and the other with fluorescent green paint, were made ready for use to mark the end and beginning of the oil spill. Intentions were to notify the bridge of both events, in order that Loran "C" fixes could be obtained to facilitate finding the oil on a return pass.

An electrically powered gear pump, which we had intended to use to spray the oil into the water from the stern of the ship, was found to be inoperable, just prior to the beginning of the

test. Moreover, the two 400-Watt spotlights which we had intended for use as main sources of UV illumination, were discovered to be almost completely deficient in UV, apparently due to incomplete removal of phosphor material from these bulbs.

It was decided, therefore, to lay the oil spill by simply pouring the oil through a jury-rigged sieve (made of plastic buckets with holes punched in the bottoms of these), over the stern into the wake of the ship. The sole source of illumination available for fluorescent lighting was the Hanovia 565-Watt sun lamp, which emitted a very large percentage of its light in the form of visible white light of rather high intensity; this lamp was mounted on the fantail, with the light being directed to port and starboard by swivelling the lamp component in these directions.

At the commencement of the exercise, the green plastic blanket was thrown as far aft into the wake as possible; unfortunately, the blanket was caught in eddies of the wake, requiring considerable attention to prevent fouling of the ship's screws. In the confusion of the moment, no notification was given to the bridge of the moment when oil spill was initiated, nor at the completion of the oil spill (although the red fluorescent blanket was successfully deployed shortly thereafter); thus, no Loran fix was obtained. It was estimated that the duration of the oil spill was approximately three minutes, for an estimated length of oil track of about 0.3 mile.

The bridge was notified several minutes after completion of the spill, and a Williamson turn to port was executed to attempt a return pass with the oil slick estimated to be to port by about 25 feet. The UV light was directed to the port beam, and several minutes later the red fluorescent marker was clearly observed passing to port by about 25 feet. About 100 yards astern of the marker the oil spill was clearly discernible, as a brightly fluorescent ribbon of about a foot in width, extending for about 300 feet. Several separated patches of fluorescent oil were also clearly visible in the contiguous areas of this track,

undoubtedly arising from turbulence effecting separation of the spill into discrete patches.

At the same time the oil spill ribbon was observed by fluorescence, the operators of the Datasonics acoustic sensing gear reported sonar signals from globular material near the surface of the water in the precise vicinity of the oil spill.

After passing the spill area, another Williamson turn was executed, this time with intention of crossing the oil spill track (the precise location of the spill was recorded from Loran fixes during the previous passing maneuver). No fluorescence was detected, definitively, although small patches of fluorescence were reported by separate observers, each such report being unconfirmed by others, however, during the period of time the ship was in the vicinity of the previously fixed location of the spill. Simultaneously, during this period of time, the operators of the Datasonics acoustic sensing gear reported enhanced sonar signals from globular material descending from the surface. It appears that the dense fish oil (density = 0.926, not much less than that of sea water, or 1.025), of significant water solubility due to polar carboxy and olefinic character of its components, was mixing with and falling from the surface of the water. This tended to be confirmed in a final pass over the area, at which time the acoustic signals were again strongly detected at significantly lower depths and with greater dispersion.

Because of the short notice of availability of the ship for this test, high speed photographic equipment could not be obtained for the test. Conventional photography was attempted, but illumination from the fluorescent spill area was not sufficient for this (although the spill area was very easily discernible to the unassisted eye, and more than enough so to provide adequate visibility for night-time oil spill control and recovery operations).

CONCLUSIONS

In spite of equipment breakdowns, inadequacies and confusion

as may be expected in any initial extrapolation of system testing from small lab bench to full field scale, excellent results were obtained in this test, indicating that if water dispersible, oil soluble fluorescing agents can be efficiently distributed in small concentrations over open water surfaces with floating oil patches, then sufficient visibility will result from fluorescent illumination from conventional UV sources to enable night-time oil spill control and recovery operations. It is even possible that, with such a system, discernibility of perimeters of oil patches may be greater than is the case in conventional day-time operations, in which it is often very difficult to locate such oil patches.

Very considerable synergistic effect is realized on combination of this system with environmental underwater acoustic sensing gear, whereby dispersion of the oil into the near surface can be detected along with surface contaminants.

Future tests should be conducted with emphasis on the following:

1. Use of more powerful UV illumination (e.g., with conventional high powered UV lamps of 2000 Watts or more intensity), perhaps on several auxiliary craft stationed around a given site, to permit considerably larger area coverage than was attainable in this initial operation involving a primitive UV lamp which enable illumination of patches up to 50 to 100 feet away from the ship.
2. Further studies of the combined fluorescence/acoustic sensing systems, particularly in applications over wider areas.
3. Delivery of fluorescer from helicopters or fixed wing aircraft, onto open water areas with floating oil patches. It is anticipated that such delivery would occur several hours prior to subsequent night-time oil spill control or recovery operations, utilizing UV-induced fluorescent illumination. For such testing purposes, it is suggested that aircraft delivery occur

during late afternoon hours, although such delivery could occur at night as well.

Particularly in terms of the proposed aircraft delivery test in which a significant time interval will exist between delivery of the fluorescer onto the oil, and subsequent detection at night, it is strongly suggested that EPA and Coast Guard permission be obtained for use of hydrocarbon rather fish oil in formation of the slick. The results of this exercise indicate that fish oil of high density and significant water solubility will not persist on a water surface for enough time to permit surface detection several hours later. It is judged likely that vegetable oil would behave similarly. Several experienced observers on board the ship for this test have expressed similar opinions.

ACKNOWLEDGMENTS

Grateful acknowledgment is extended to Captain Dwight Paine and the other fine crew members of the EPA Ocean Survey Vessel ANTELOPE, without whose efforts and assistance this exercise could not have succeeded; and to the United States Environmental Protection Agency (represented at this test by Mr. Edward S. McLean) and the Mar Corporation of Rockville, Maryland (represented at the test by Dr. Leslie Pierre) who made the ANTELOPE available for the test, and who provided valuable technical advice and assistance prior to and during the test.

We are also grateful to the Massachusetts Maritime Academy, and its Director of Fisheries Programs, Dr. David Kan, for the cooperation and assistance generously provided for many years to this group; and to William A. Curby, Director of the Sias Memorial Research Laboratories of the Lahey Clinic of Burlington, Massachusetts who has materially shared in the development of the fluorescence process from the concept to implementation stages.

The contributions by Dave Porta and Bill Dalton of Datasonics, Inc. in the synchronized utilization of Datasonics acoustic

sensing equipment, and in interpretation of acoustic data, were of obviously great importance in this test. Their innovative approaches and enthusiastic support is greatly appreciated by this group.

I wish to acknowledge also the following students without whose industry, ideas and enthusiasm this project work would not have been possible, and who have made this work as enjoyable as it has been: Alberto and Juan Benevides, Brian Daigle, Gene and Jim DiPoto, Samir Mody, Kingsley Ndi, Stephen Quigley, Manan Shah, Son Truong, and Ronald Verna. Dr. Albert Donatelli of the Chemical Engineering Department at the University of Lowell contributed valuable advice and assistance to us, also.

The University of Lowell Alumni Association provided funds for the support of students working on this project during the Summer of 1981, during which time this project was brought to its present successful status, and the students and I are very grateful to the Alumni Association for this generous support. Finally, I wish to express my thanks to the GTE-Sylvania Corporation for the donation of equipment, the technical advice and assistance extensively provided to us, and the encouragement at all steps expressed to us. Mssrs. George Duggan, Robert Edelson, Joel Finkel, Charles Morse, and Paul Ulcikus of GTE Laboratories and GTE-Sylvania were especially helpful to us in this regard.

APPENDIX I

PROPOSED OIL AND HAZARDOUS CHEMICAL SPILL CONTROL AND RECOVERY BY AMINE CARBAMATE GELATION

Principal Investigator: William W. Bannister
Department of Chemistry
University of Lowell
Lowell, Massachusetts

ABSTRACT

Hazardous chemical spills on water surfaces pose serious problems in terms of both water-borne and air toxicity effects, and, in the case of flammable materials, fire hazards. These problems are of particular and immediate concern to personnel involved in spill control and recovery operations, with obvious requirements for extremely close contacts by these individuals with the hazardous chemicals.

Our group has had several successful projects with the EPA and the Navy, in the development of a process whereby oil and hazardous chemicals on water surfaces can be gelled to a solid consistency quickly, safely and economically using dehydroabietylamine (Amine DTM) sprayed in low (ca.16%) concentrations onto the oil, with subsequent treatment with carbon dioxide to form the carbamate as a gelling agent. The gelation process has been shown to reduce volatilities in open air by 50% or more, with corresponding reductions in toxic and fire hazards. Moreover, the process is compatible with fluorescent agents, which our group has demonstrated to thereby provide considerably extended capabilities into night-time operational hours. (In this latter process, cheap, non-toxic and highly efficient fluorescent agents soluble in organic spills and dispersible into the underlying water column are applied in extremely low concentrations over the spill area; in open water with no oil or chemical present the agent is quickly dissipated into the water, but is retained wherever oil or chemical spills are present. At night UV light can then be beamed over the spill area with illumination by resulting fluorescence from the slick areas permitting easy discernment of these areas and thus providing excellent capability for night-time recovery and control work.)

In a recent field test at the US Navy Submarine Base at New London, CT an actual oil spill was successfully controlled and recovered quickly and efficiently using a prototype trimaran craft equipped with a CO₂ transit tank, several barrels of Amine D, and easily constructed disposable spraying equipment.

It is now proposed that a portable, easy-to-assemble-and-disassemble trimaran craft for use in oil and hazardous chemical spill recovery and control operations on inland waters and in harbor situations, be constructed. The craft will be capable of supporting a load of approximately six (6) tons in shallow (less than two feet deep) waters. Up to 2,200 gallons of oil or chemical spill can be controlled and recovered in an area of one acre (43,650 ft²) in a track up to 17 feet wide and one half mile in length, in about five minutes. Equipment for operation with fluorescent agents under night-time conditions can easily be installed on the craft. The craft would be capable of being assembled and disassembled in about two hours, and when disassembled can be stored and transported in a truck trailer of about 8'X12'X6', along with all required chemicals, supplies and equipment.

OBJECTIVES AND STATEMENT OF WORK

It is proposed to design, construct, test and operate a modified version of the prototype trimaran raft illustrated in figures 39-40 of this report. The following trimaran will have the following features:

1. The raft would have, when assembled, a platform area of 12' X 24', resting on three collapsible pontoons, each 33" in diameter and 24 feet in length (with three watertight sections in each pontoon for safety purposes. The pontoons would be fabricated as a 3/4" shell in the form of two sections with hemicircular crosssections which will be bolted together, and with circular lids to complete an enclosed cylindrical shape. Inside each pontoon, prior to bolting together, will be placed an inflatable rubber tube; after inflation, the pontoons will then be watertight structures. During storage and shipment, the pontoon assemblies will be nested together to provide minimal storage requirements. Assuming a freeboard of half the diameter of the pontoons, these would displace (and thereby support a total loading of) 13,275 pounds in fresh water.
2. A "box-spring" type of assembly of steel or aluminum braces as indicated in the schematic diagram presented in Fig. A in this enclosure will lie under and above the pontoon, with steel hoops secured to this framework through which the pontoons would be inserted, and then braced together.

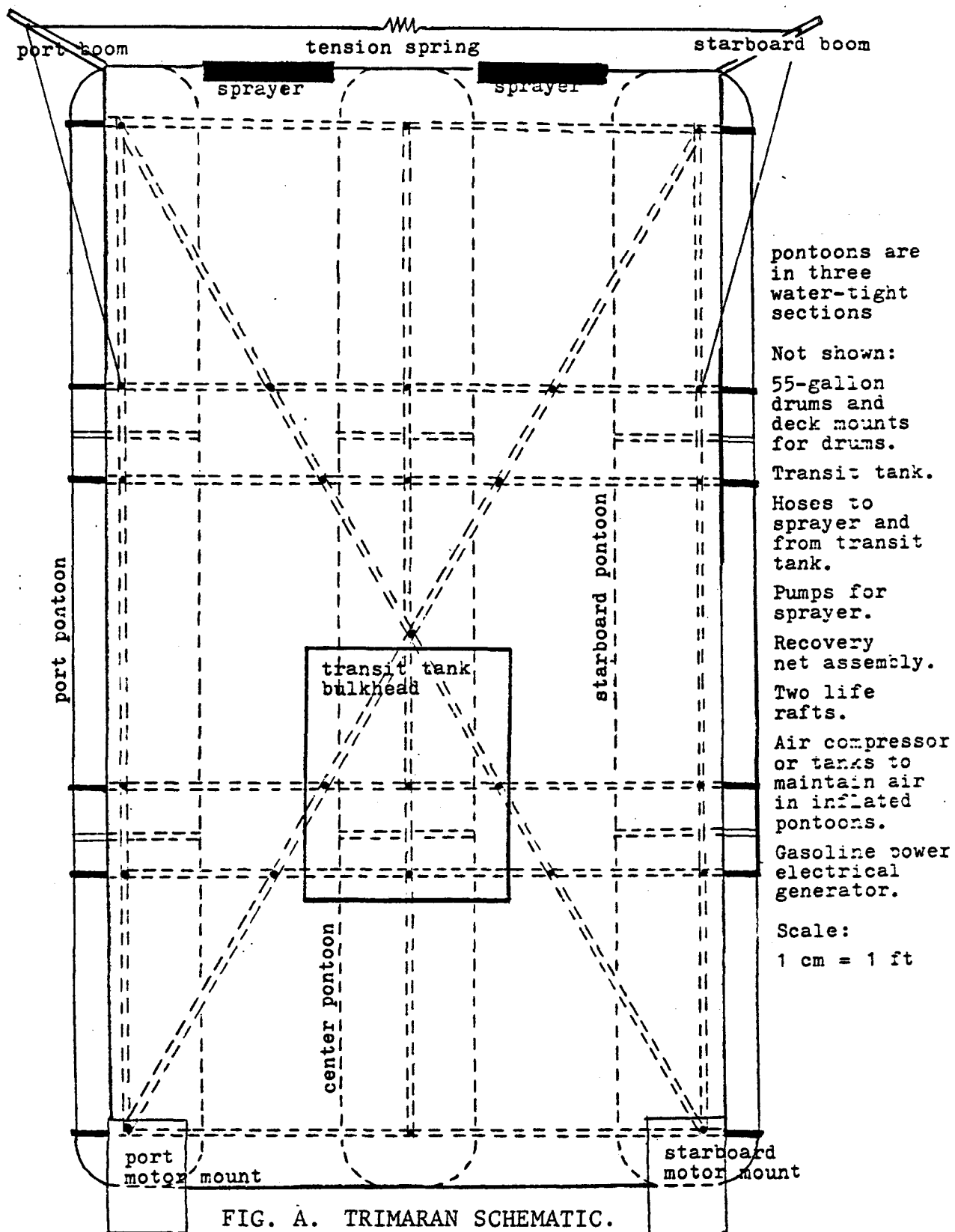


FIG. A. TRIMARAN SCHEMATIC.

Where launching from a boat ramp will be feasible, casters on the base of the platform frame will facilitate movement of the craft. Threaded lugs projecting upward from the lengthwise and transverse frames will match with pre-drilled holes in transverse and diagonal frames, and with holes in 4' X 8' marine plywood deck sections, which will then be

secured by lug nuts by means of a pneumatic lug wrench powered by CO₂ from the craft's transit tank. Eye bolts shall be secured in the frame, extending above the deck to permit crane launching in the event of non-availability of a boat ramp.

3. Break-away bulkheads (for quick release in the event of emergencies requiring overboarding of heavy items on deck) shall be located in strategic locations on deck plates to provide secure clamping of the transit tank, 55-gallon Amine D drums, and other items otherwise apt to move uncontrollably as a result of wave action.
4. Port and starboard booms, hinged at the bow of the trimaran and held taut by means of adjustable cables under spring tension. These booms serve to increase the flow of water (and surface oil) into the spaces between the pontoons, in which spraying and carbonation to effect gelation take place. In certain instances involving a moving contaminated stream of water, these booms could conceivably be extended from banks of the stream to the moored trimaran gel craft, to enable treatment of the entire surface area of the stream.
5. Disposable sprayer heads, constructed of pre-drilled 3½ foot PVC pipes, are located just forward of the channel intakes between the pontoons.
6. Two variable speed heavy duty metering pumps force Amine "D" solution from 55-gallon drums located in close proximity to the pumps and sprayers, through polyethylene tubing (1" diameter). (Pumps, drums and drum mounts, and feed tubing are not shown in Figure A. Eight drums can easily be accommodated on the deck space in the forward end of the gel craft, providing for treatment of 2,200 gallons of surface contamination, which would present a spill area of an acre in the event of a 2 mm slick.
7. A transit tank with a capacity of 700 pounds of liquid CO₂ is located abaft the center of the gel craft, in a position calculated to provide reasonable average stability. The transit tank is held in place by a bulkhead with breakaway sections, to enable immediate overboarding in the event of imminent capsizing of the craft.

8. Carbonator hoses extend from the transit tank forward to positions slightly abaft the sprayers, at which points these connect to sparging fingers extending to the rear, under the deck plating and between the pontoons. When activated, the tank discharges liquid CO₂ into the sparging fingers which expel this into the stream of mixed ammine and contaminant moving aft between the pontoons.
9. Two 25-HP marine outboard engines are situated at the stern of the trimaran, providing propulsion and steering for the craft.
10. For night-time operations, two high-intensity marine spotlights can be mounted on stanchions at the bow of the craft, for use with fluorescent agents.
11. Cloth after chutes extend behind the two channels between the three pontoons. These serve to provide prolonged contact time between the CO₂ and amine/oil mixture, to optimize gelation, and to conduct the gelled oil or hazardous chemical into nets located at the end of the chutes.
12. Auxiliary equipment on board will include a gasoline powered electrical generator, compressed air tanks to maintain air pressure in inflated pontoons, on an as-needed-basis, fire extinguishing equipment, a repair locker equipped with patching supplies and other damage control equipment, and overhead frames to support transparent polythylene tarpaulins in the event of inclement weather (where wind conditions would permit such use). GFI (Ground Fault Interrupter) equipment shall be installed on the trimaran. When in the water, two three-man life rafts shall be deployed alongside the trimaran. All crew personnel shall be equipped with life jackets while on board, at all times. Sturdy railings shall be installed on the periphery of the deck.
13. Advice shall be solicited from qualified US Coast Guard authorities throughout the design, construction and testing phases of this project, to ensure that the craft will be seaworthy and safe to operate. All phases of construction shall be undertaken in consultation with a qualified marine engineer and naval architect.

PONTOON DISPLACEMENT, AND LOADING REQUIREMENTS

Assuming 24-foot lengths for each of the pontoons, and 33" diameters, with half of the pontoon assembly to be available for freeboard (i.e., above water elevation), the three pontoons would thus displace 13,275 pounds of fresh water, or 13,600 pounds of sea water.

The following estimates are provided by way of suggested loading requirements:

| | | |
|---|------------|---|
| Pontoon weight (for nine pontoons): | 750 pounds | |
| Raft and bracing for raft: | 1,200 | " |
| Transit tank and carbonator hoses: | 2,000 | " |
| Metering pumps: | 600 | " |
| Sprayer assemblies: | 200 | " |
| 8 55-gallon drums of Amine "D" solution | 4,100 | " |
| Booms: | 200 | " |
| 2 25-HP marine engines; | 200 | " |
| Assorted gear: | 500 | " |
| Generator: | 280 | " |
| 6 Crew personnel: | 1,200 | " |
| TOTAL | 11,230 | " |

Excess displacement
available before
decreasing 16½" free
board requirement:

2,045 pounds (fresh water)

2,370 pounds (Sea water)

PROJECTED MATERIAL AND SUPPLIES REQUIREMENT

*Raft Assembly:

- *9 4' X 8' marine plywood
- *3 pontoons
- *Booms, tension cables
- *Steel bracing
- *Stanchions, railings
- *Frame and tarpaulin

Amine "D" drums, 55gallons; eight

Transit tank rental

Ball valves for tansit tank

2 25' carbonator hoses

CO₂

Drum rack and bracing

It is believed that most or all of the following equipment and supplies requirements can be fulfilled by resources available to this group:

Pumps: 2 metering, high capacity

Electric generator

Hoisting crane (one ton capacity)

Pnuematic impact wrench

**Crop duster aircraft charges

Asterisked items pertain to fluorescent night-time visibility capabilities, if desired.

**Fluorescer

**UV illumination equipment

PROPOSED
USE OF FLUORESCENT AGENTS AND ACOUSTIC SENSING FOR NIGHT-TIME HAZARDOUS
MATERIAL SPILL RECOVERY AND CONTROL OPERATIONS

Principal Investigator: William W. Bannister
Department of Chemistry
University of Lowell
Lowell, Massachusetts 01854

ABSTRACT

Oil and hazardous chemical spills pose serious problems in terms of the very poor visibility often attending such situations. No operational capability exists at night or in other periods of low visibility, when operating personnel are unable to discern spill boundaries. However, time is extremely important in spill control and recovery work; in the space of a few hours areas cleared of an oil spill by skimming or similar operations can be covered again as unharvested oil drifts back over the cleared track. Moreover, skimmers are most efficient with thicker oil films; spreading of oil not only increases the operational area, but also decreases film thicknesses with attendant decrease in efficiency of the effort.

We have previously demonstrated that commercially available, non-toxic and highly efficient fluorescent agents with both oil and water compatibility can be applied in very low concentrations to oil spills with excellent results. In open water areas the agent is dissipated into the water column, but is preferentially retained in any oil patches on the water surface. At night, when natural light has sufficiently diminished to permit visibility of fluorescent light, UV light is beamed over the spill area with illumination by resulting fluorescence occurring only from the oil spill patches, thereby enabling easy discernment of the perimeters of such areas and thus extending operational capabilities into night-time hours. This would be particularly important in situations occurring in winter months in higher latitudes when night-time conditions are significantly more prolonged than are daylight conditions.

In our previous work we have demonstrated also that very considerable synergistic effects are realized on combination of the fluorescence technique with environmental acoustic sensing gear, whereby dispersions of oil into the near water surface can be detected along with surface oil.

We now propose to perform full-scale tests with application of the fluorescer in a dilute spray delivered either from ships or from aircraft, over wide open water oil spills, and in other tests in the form of mixtures fluorescer and finely powdered limestone delivered as a dust from aircraft. In all cases conventional skimmer craft equipped with UV flood light, and acoustic sensing gear operated from such skimmer craft will be utilized to attempt oil spill reconnaissance operations.

SUMMARY OF PROJECT PHASES

PHASE I. FEASIBILITY TESTING

A. Feasibility Testing (June 1 - September 14, 1981)

This work, culminating in the September 14 ANTELOPE sea trials, served to demonstrate the feasibility of use of fluorescent illumination and acoustic sensing as a means of providing a night-time capability for oil spill recovery and control operations. Cf. preceding discussion and Appendices B,C,D and E for details pertaining to this work.

B. Design and Construction of Spraying Equipment, and Investigation of Improved Fluorescent Formulations (September 1, 1981 - June 30, 1982)

Support for this work has been provided by GTE/Sylvania, Incorporated. The emphasis of this work is in the design of shipboard equipment for those situations in which aerial delivery systems may be inappropriate (e.g., in congested harbor situations), and in investigations of various fluorescers in powdered limestone or other inert formulations for dusting operations.

With regard to new fluorescent agent systems we are currently investigating fluorescers provided by the Morton Chemical Co. of Paterson, New Jersey which have significant solubilities in hydrocarbons and which may be better suited than stilbene derivatives for this work.

PHASE II. SYSTEM DESIGN AND OPERATIONAL TESTING OF EQUIPMENT

A. Shipboard UV Illumination Systems

No difficulties are anticipated in regard to design and installation of suitable UV illumination sources for use on shipboard. We anticipate a requirement for several tests to determine the number, proper positioning, and overall intensities of the lamps to be used in the final test exercises, and thereafter for routine use. It is deemed advisable at this early moment to consider the positioning of such lamps as high in the ship as possible, to minimize sea-scatter effects and to achieve as wide a coverage as possible, with lamps to be directed forward and aft with maneuverability port and starboard.

We intend to consult extensively with the GTE/Sylvania Corporations' technical personnel with regard to design, installation, and operational sub-phases.

B. Aerial Devlivery and UV Illumination Systems

Conventional crop dusting techniques and apparatus, as are available through a variety of firms in this area,

are deemed adequate at this point for delivery of the fluorescer agents onto spill areas.

The same considerations for UV illumination will apply in this sub-phase as for the shipboard installations discussed in the previous section.

C. Near-Surface Water Column Profiling By Acoustic Sensing As A Complementary Means of Detecting Extents of Low-Visibility Oil Spills

Datasonics, Inc. will serve in this study to track and map concentrations of near-surface concentrations of suspended oil in the water column, as an adjunct means of detecting otherwise indiscernable (e.g., due to night-time or other low-visibility conditions) oil spills. This techniques, moreover, will provide a gauge as to the rate and extent of dissipation of surface slicks. The Model DFS-2100 Environmental Echo Sounding System is a specialized dual frequency system designed for this application. Operating from 3 to 300 khz, the system makes use of precisely controlled and measured transmitted and received signal levels to allow quantitative measurement of echo levels produced by scatterers throughout the water column. Use of a stabilized narrow beam transducer provides extremely good resolution of discrete scatterers associated with thermal or salinity changes, and other natural processes which produce a density gradient.

(Reference is made to the last page of Appendix F to this proposal, which illustrates the type of signal provided by hydrocarbon suspensions in the water column in acoustic sensing; the signal is best seen in the upper left quadrant of this chart.)

Datasonics equipment also includes high resolution high powered low frequency, and general purpose sub-bottom profiling systems with towed vehicle, "over-the-side" and "in-hull" transducer installations.

D. Description of Proposed Exercises

It is proposed that an area of about 3,000 feet by 330 feet (about 23 acres) in open water areas of Cape Cod Bay, or South of Buzzards Bay off the coastline of Massachusetts, be utilized for both preliminary and final tests.

The preliminary tests will probably require four separate days, during which exercises the various sonic and fluorescent effects and parameters discussed previously will be studied singly and then jointly, under various weather and wave conditions, varying concentrations of fluorescer, and varying intensities of UV light.

After preliminary testing has been accomplished, the overall fluorescent/sonic systems will be tested in a final two-day exercise, again under varying conditions, as a means of providing a "real-life" demonstration of efficacy of the systems. For the final test exercises the services of the EPA OSV ANTELOPE will be sought, in view of the excellent research and monitoring capabilities of this vessel.

Application of fluorescer agents will be tested both preliminary and final exercises by aircraft dusting operations. Ship-board systems will be studied, also. For these purposes the services of a commercial crop dusting firm are recommended, in view of the equipment and expertise such a firm would possess for accurate and even distribution of the agent. For spray purposes, a volume of about 250 pounds of a fluorescer formulation, comprised of about 8% of fluorescer suspended in powdered gypsum or limestone, is recommended for the test, representing a dose rate of about ten pounds per acre. Smaller volumes of correspondingly higher concentration could be utilized, as well. It is anticipated that the test area will have light to moderate coverage (though more extensive spill coverage would be satisfactory, also) by 2 mm. oil slicks, of any composition (light, medium or heavy refined, residual or crude stocks) as may be routinely encountered in the harbor area. Assuming even distribution of the agent over the test area, oil patches would then have an applied concentration of the agent in the oil of about 0.007% (70 ppm). From previous test results, it is anticipated that fluorescer applied to open water (lacking oil coverage) would be effectively dissipated into the water column within one hour after spraying; for oil patches sprayed with the fluorescer solution, it has been found that there is very little extraction of the fluorescer into the water--after three days, more than 98% of the fluorescer is still retained in the oil.

An ideal time for application would be about 4PM, thereby enabling adequate differentiation of oil slick perimeters shortly after nightfall, some four or five hours later. Dusting could be accomplished in night-time operations, however, and this would probably be a requirement for preliminary tests in which we would intend to use vegetable or fish oil simulants. For the final test operations it would be highly desirable to utilize at least one hydrocarbon type of spill, in view of the inadequacies (high density and high dispersability of the simulant oils) which would probably prevent day-time dusting followed by UV/sonic monitoring several hours later. For most tests it is suggested that clear weather (for both day and night phases) and low wind speed (for the afternoon aerial application) conditions be sought. Moreover, it would be desirable to choose a date during which there would be minimal surface movement of the

sprayed area (e.g., due to tidal effects) between the time of application and that of the night-time recovery effort. Alternatively, use of untethered fluorescent markers, dead reckoning calculations, or other means should be employed to provide as much knowledge as possible regarding movements of the sprayed area.

When deemed sufficiently dark for the recovery phase of the overall operation, it is then suggested that a DIP 3001 Self-Propelled Harbor Skimmer (or equivalent) be deployed, especially equipped for this test with two 1000-Watt mercury UV lamps without filters, to operate continuously during the overall test exercises. Conventional visible illumination is afforded by these lamps, in addition to UV radiation, to afford adequate navigational capability in the steering of the craft; at the same time, the enhanced UV-fluoresced visible light from the oil patches will provide ample means for full discernment of slicks on the water surface. In order that wider-range fluorescence can be achieved, thus providing full capability for overall evaluation of the recovery effort, it is proposed that a helicopter equipped with a rack of six 72" 85-Watt UV fluorescent lamps fly overhead to one side of the slick area (to avoid downdraft effects on the slick area), with radio communications between the helicopter's observer team and the skimmer craft crew. With this capability the skimmer could be guided from patch to patch.

At the suggestion of Dr. William Garrett of the Naval Research Laboratories, it is also proposed at this time to use a surface collecting agent (e.g., Navy Piston Film) with a vividly colored fluorescer incorporated in this agent's formulation, thereby further facilitating the collection and control effort.

Recording of all events by motion picture and/or by video, and still photography would be highly desirable, during both afternoon and night-time evolutions (the latter obviously requiring rather sensitive film stock).

ANTICIPATED HAZARDS

TOXICITY: No significant hazards are anticipated. The fluorescent agents which would be used are widely used additives in many household detergent formulations, with full approval by the FDA. The LD 50's for such agents are typically about 10,000 mg/kg bodyweight for test animals in the acute dosages, an index of quite low toxicity; in the terms of chronic exposures (i.e., on a continuous basis) of 1.000 ppm no observable effects are noted in test animals over one and two year periods. No skin irritations in human subjects are noted for such agents.

UV

RADIATION: No hazard is anticipated from UV radiation from the helicopter rack, in view of the anticipated altitude (100 feet or more); speed, motion and typical distance of the helicopter from the skimmer craft, of 100 yards or more; and low intensity of radiation. These lamps are routinely used in outdoor and indoor advertising, entertainments, and similar applications with no required eye protection. In as much as these lights will be projected downward with no upward illumination, aircraft crew will not be exposed to this radiation at all. The more powerful 1000 Watt lamps contemplated for use on the skimmer would present an eye hazard for personnel experiencing constant radiation within a distance of 100 feet. These lamps are therefore proposed for mounting on bowsprit assemblies extending twenty feet in front of the skimmer, with beams directed forward and downward on the water in front of the boat out to a distance of 100 feet, and with complete shielding in back of the lamps to prevent any radiation onto the skimmer itself.

All personnel working with this project will be issued goggles to be worn in the event of accidental misalignment of lamp beams; and all UV sources will be deenergized in the event of such accidental misalignment.

No serious UV hazards are anticipated.

| TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing) | | |
|---|--|---|
| 1. REPORT NO. | 2. | 3. RECIPIENT'S ACCESSION NO. |
| 4. TITLE AND SUBTITLE NEW TECHNIQUES FOR FLOATING POLLUTANT SPILL CONTROL AND RECOVERY. | | 5. REPORT DATE August 15, 1983 |
| | | 6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S) W.W. Bannister, W.A. Curby, D.L. Kan, W.J. Dalton, D.A. Porta, and A.A. Donatelli | | 8. PERFORMING ORGANIZATION REPORT NO. |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Lowell, Lowell, MA 01854; Sias Labora- tories, Lahey Clinic Foundation, Burlington, MA 01803 Massachusetts Maritime Academy, Buzzards Bay, MA 02532; Datasonics, Inc., Cataumet, MA 02534 | | 10. PROGRAM ELEMENT NO. CBRD1A |
| | | 11. CONTRACT/GRANT NO. EPA Project Nos. R806118 01 and R804628 01 |
| 12. SPONSORING AGENCY NAME AND ADDRESS Municipal Environmental Research Laboratory--Cin., OH Office of Research & Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268 | | 13. TYPE OF REPORT AND PERIOD COVERED Final, 9/15/78-9/14/79 |
| | | 14. SPONSORING AGENCY CODE EPA/600/14 |
| 15. SUPPLEMENTARY NOTES Project Officer: Uwe Frank (201) 321-6626 | | |
| 16. ABSTRACT Hazardous material (HM) spills pose serious problems in terms of the very poor visibility often attending such situations. No operational capability exists at night or other periods of low visibility. However, time is very important in spill control and recovery work; in a few hours, areas cleared of an HM spill can be covered again as unharvested HM drifts back over the cleared track. Moreover, skimmer operations are most efficient with thicker oil films; spreading of oil not only increases the operational area, but also decreases film thicknesses with attendant decrease in efficiency of the effort. This report discusses new techniques whereby (1) HM spills can be gelled quickly and completely to a solid consistency. The gel is of much greater visibility; does not readily flow or spread; is easily, quickly, and completely recovered by nets; has lower volatility and lower fire and toxicity hazards; does not permeate into porous materials; and is easily regenerated into the original HM and gelling components. (2) Cheap, nontoxic and efficient fluorescent agents can be applied in low (50-ppm) concentrations onto spills by conventional crop-dusting or spraying techniques. Where there is open water with no HM cover, the fluorescer is dissipated into the water, but is preferentially retained wherever there are HM patches. At night, illumination by UV light (modified mercury vapor street lights) can be beamed over the spill area. Vivid fluorescent illumination occurs only from the HM patches, providing night-time control and recovery capability. (3) Underwater sonic sensing provides excellent synergistic effects with the fluorescence technique. | | |
| 17. KEY WORDS AND DOCUMENT ANALYSIS | | |
| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
| Acoustic Sensing Environmental Techniques; Amine Carbamates; Amine D; Amine Gelants; Beach Protection; Fire Hazard Reduction; Fluorescers; Gelation; Hazardous Material Spill Control; Hazardous Material Spill Re- covery; Night-Time Operations; Sonic Sens- ing Environmental Techniques. | | |
| 18. DISTRIBUTION STATEMENT Release to Public | 19. SECURITY CLASS (This Report) Unclassified | 21. NO. OF PAGES |
| | 20. SECURITY CLASS (This page) Unclassified | 22. PRICE |